

## DESCRIPTION

THERMALLY EXPANDED MICROSPHERE, PROCESS FOR PRODUCING THE SAME,  
THERMALLY EXPANDABLE MICROSPHERE AND USE THEREOF

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## Technical Field

[0001] The present invention relates to heat-expanded microspheres, a production process thereof, heat-expandable microspheres, and application thereof. More specifically, the present invention relates to heat-expanded microspheres, which have a particle size distribution with a coefficient of variation showing a minimum difference before and after heat expansion, and which contain slight ratios of aggregated microspheres and microspheres of high true specific gravity (microspheres not having been expanded to a prescribed degree); a production process thereof; heat-expandable microspheres, which contain slight ratios of aggregated microspheres and microspheres of high true specific gravity, are resistant to damage from external force, prevent the hardening and shrinkage of porous material compositions for weight reduction in molding processes, and solve the problem of time-dependent thermal deflation; and the application thereof.

[0002] In the present invention, the heat-expandable and heat-expanded microspheres in which a specific fluorine compound is encapsulated, are filled in a cavity of a tire-and-rim assembly, as a superior sealing material and internal pressure supplier when the tire is damaged.

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## Technical Background

[0003] Heat-expandable microspheres comprising a structure of a shell of thermoplastic resin and a blowing agent encapsulated therein are generally called heat-expandable microcapsules. Vinylidene chloride copolymers, acrylonitrile copolymers, and acrylic copolymers are usually employed as the thermoplastic resin, and hydrocarbons, such as isobutane and isopentane, are mostly employed as the blowing agent. (Refer to Patent Literature 1.)

[0004] Such heat-expandable microcapsules are processed into lightweight hollow particles (heat-expanded microspheres) with heating and expanding. A process for spraying a dispersion of heat-expandable microcapsules in hot gas to expand and dry the microcapsules simultaneously has been proposed as a process for expanding heat-expandable microcapsules. (Refer to Patent Literature 2.) The process, however, has a problem, in that the deposition of aggregated microcapsules at the end of the spray used is highly likely.

A process for producing hollow particulates by expanding heat-expanding microcapsules, which have been produced by impregnating the same with a blowing agent, in hot gas from an electric hot gas generator has been proposed. (Refer to Patent Literature 3.) As described in comparative example 3 in Patent Literature 3, the process completely failed to produce particulates having preferable properties, when the process was applied to expand heat-expanding microcapsules in which

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a blowing agent was encapsulated, because the process could not control the retention time of each heat-expandable microsphere in the device, and the resultant hollow particulates had low expansion coefficients and shrunk.

[0005] Further, a process for producing porous particulates wherein dried heat-expandable microspheres on a belt conveyer are heated and expanded at a temperature higher than their expanding temperature and transferred from the conveyer with air flow has been proposed. (Refer to Patent Literature 4.) The process has a problem, in that non-uniform product is possibly produced due to varied true specific gravity and increased coefficient of variation in particle size distribution of resultant porous particulates, both of which result from unexpanded heat-expandable microspheres migrating into expanded porous particulates being transferred with air flow.

[0006] It is preferable to minimize the generation of aggregated microspheres, usually by decreasing the quantity of remaining raw material, heat-expandable microcapsules, in the expanding operation of the heat-expandable microcapsules. In order to meet such requirement, expanding each of heat-expandable microcapsules with the same heat history is considered essential.

For example, a process for expanding microcapsules wherein heat-expandable microcapsules are expanded in an aqueous slurry, and the slurry containing expanded particles is passed between grinding stones to disperse aggregated particulates, has been proposed. (Refer to Patent Literature 5.) Although the process can apply the same heat history to all of heat-expandable microcapsules, the fusion of expanded microcapsules appears as a problem when the expanded microcapsules need to be dried for blending in plastics, paints, rubber, and sealants, being different from employing the aqueous slurry.

[0007] A process for producing porous particulates wherein heat-expandable microspheres are heated and expanded after being dispersed into a slurry has been proposed. (Refer to Patent Literature 6.) The process can also apply the same heat history to all heat-expandable microspheres. But the process has problems, in that there is a low production efficiency due to the steps of deliquoring slurry containing expanded heat-expandable microspheres and drying, which are required for producing dried hollow particulates, and possible coagulation of hollow particulates, especially those produced from heat-expandable microspheres having shells with low softening points, at the drying step.

[0008] Heat-expandable microspheres, which have particle sizes distributed in a sharp peak, and their production process, have been proposed. (Refer to Patent Literature 7.) The literature discloses that the heat-expandable microspheres produced in the process expand sharply into expanded microspheres of uniform shape and size, though the expanding procedure is not clearly specified. Although the heat-expandable microspheres have uniform particle size distribution, it is apparent to those skilled in the art that expanded microspheres of uniform particle size distribution without aggregated microspheres cannot be produced in the known conventional expanding processes.

[0009] As clearly described above, it is required to minimize remaining raw material and the

generation of aggregated microspheres in both dry and wet expanding processes, though it has not been attained at present.

[0010] Hollow particulates are blended in porous molded products in order to lighten the products as described above. Porous molded products are usually produced by mixing and kneading a base component, filler, and hollow particulates to prepare a porous material composition, and by molding the composition into a prescribed form. In the mixing and kneading process, hollow particulates are often subjected to great external force which damages a portion of the particulates, and it leads to a problem, which is the unattainable lightening of a product to a prescribed level. In addition, thermoplastic resin forming the shell of hollow particulates is softened with heat and pressure applied to the porous material composition in the molding process, and the hollow particulates are subjected to external pressure. The internal pressure generated by the vapor of the blowing agent encapsulated in the hollow particulates cannot resist the external pressure, and thus the hollow particulates shrink to some extent in the molding process. As a result, there are problems with the hardening and shrinking of products, such as shrunk porous molded products, poor dimensional stability, and unattainable lightening of a product to a prescribed level.

[0011] For solving those problems, a porous material composition in which heat-expandable microspheres and hollow particulates are blended has been proposed. (Refer to Patent Literature 8.) Although the hardening and shrinking are solved with the composition, it requires a complex step of preparing two different particles (heat-expandable microspheres and hollow particulates). In addition, porous molded products are thermally deflated with time, resulting in the decrease of their volume when used at high temperature, though such deflation is not remarkable when they are used at normal temperature. The cause of the deflation is considered to be the time-dependent leakage of a blowing agent encapsulated in hollow particulates.

[0012] For solving the problem, thermoplastic resins of low gas-permeability, such as acrylonitrile copolymer, are employed as the thermoplastic resin for forming the shell, though it is not enough to solve the problem.

[0013] Lightweight hollow particulates produced by heating and expanding heat-expandable microcapsules have been applied as lightening agents for resins and ceramics as mentioned above, heat insulators for thermosensitive paper and paints, bulkiness-imparting agents for nonwoven fabrics, shock-absorbers for automobile exteriors, and surface modifiers for attaining roughness on wall papers. The inventors of the present invention have recently developed novel heat-expandable microcapsules in which a specific fluorine compound is encapsulated as a blowing agent, and have found the application of porous particles produced by heating and expanding the microcapsules as a volume-retaining agent for pressure vessels. (Refer to Patent Literature 9.)

[0014] Patent Literature 1: USP 3915972

Patent Literature 2: Published Examined Japanese Patent Application, Sho 59-53290

Patent Literature 3: Published Unexamined Japanese Patent Application, Hei 8-217905

Patent Literature 4: Published Examined Japanese Patent Application, Hei 8-29245

Patent Literature 5: Published Unexamined Japanese Patent Application, Sho 62-201231

Patent Literature 6: Japanese Patent 2927933

Patent Literature 7: WO 99/37706

5 Patent Literature 8: Japanese Patent 3067932

Patent Literature 9: WO 2004/074396

#### Disclosure of the Invention

10 [0015] An object of the present invention is to provide heat-expanded microspheres, which have a particle size distribution with a coefficient of variation showing only a slight difference before and after heat-expansion, and which contain extremely low ratios of aggregated microspheres and microspheres of high true specific gravity, and to provide a production process thereof.

15 [0016] Another object of the present invention is to provide heat-expanded microspheres and heat-expandable microspheres containing extremely low ratios of aggregated microspheres and microspheres of high true specific gravity, that are resistant to damage from external force, that prevent hardening and shrinking of a porous material composition in molding when they are blended in order to lighten the porous material composition, and solve the problem of time-dependent thermal deflation of the resultant porous molded products.

20 [0017] Another object of the present invention is to provide porous molded products that are sufficiently lightened, prevent hardening and shrinking in molding, are free from time-dependent thermal deflation, and have high dimensional stability.

25 [0018] Another object of the present invention is to provide heat-expandable microspheres and heat-expanded microspheres, which exhibit superior properties as a tire damage sealant and an internal-pressure supplier for a tire when filled in the inside of a tire-and-rim assembly, to provide a production process of the heat-expanded microspheres, and to provide heat-expandable microspheres as a raw material for the heat-expanded microspheres.

[0019] For solving those problems described above, the inventors of the present invention have studied and obtained the findings as follows.

30 (1) In a specific dry process in which heat-expanded microspheres are produced by heating and expanding heat-expandable microspheres that are properly dispersed, the difference in the coefficient of variation of their particle size distribution before and after heat-expansion can be decreased, the amount of raw material and slightly expanded microspheres can be lowered, and the generation of aggregated microspheres is suppressed.

35 (2) In the production process (1), almost completely heat-expanded microspheres, and heat-expanded microspheres that are capable of re-expanding to a prescribed degree (in other words, heat-expanded microspheres having a re-expansion initiating temperature), can be produced by controlling the expansion conditions.

(3) The heat-expanded microspheres that are capable of re-expanding produced in the above (2) are also novel heat-expandable microspheres having properties which were not found in the past.

(4) In a porous material composition containing the heat-expanded microspheres having a capacity of re-expanding in the above (2) and/or the heat-expandable microspheres in the above (3), the microspheres have comparatively thick shells and are durable against rupture under external force. Those microspheres prevent hardening and shrinking of the composition in molding, prevent time-dependent thermal deflation of products at high temperature, and attain superior dimensional stability owing to their optimum heat-expanding property, etc.

[0020] The inventors have also obtained the findings on heat-expandable microspheres and heat-expanded microspheres containing a specific fluorine compound as a blowing agent as described in the following (5) to (8).

[0021] (5) A fluorine compound is preferable for its flame-retardant properties. The heat-expanded microspheres produced by heating and expanding heat-expandable microspheres in this specific process made a damaged tire runnable after its internal pressure has decreased due to damage, when the expanded microspheres were filled in a tire-and-rim assembly to test the applicability of the microspheres for running damaged tires.

(6) Heat-expanded microspheres that are capable of re-expanding and produced by controlling the expansion of heat-expandable microspheres, can be filled in a tire-and-rim assembly for running a damaged tire whose internal pressure decreased, similar to heat-expanded microspheres produced by expanding heat-expandable microspheres almost completely in the specific process. It is preferable for the heat-expanded microspheres that are capable of re-expanding, in particular, to have the ability to start re-expanding at a prescribed high temperature. Recently, tires are required to run normally even at high temperatures. It is also required that tires have the ability to supply internal pressure by re-expanding immediately after the tire is damaged and its internal pressure has decreased.

[0022] (7) Heat-expanded microspheres that are capable of re-expanding can re-expand at a prescribed high temperature if the shell of the microspheres is formed of thermoplastic resin produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group.

(8) Heat-expanded microspheres that are capable of re-expanding and which have a specific anti-blocking agent adhered to the outer surface of their shell, quickly seal damage on a tire and exhibit high performance for supplying internal pressure to the tire.

[0023] With these findings from (1) to (8), the inventors have achieved the present invention specifically described as follows.

The first production process for heat-expanded microspheres of the present invention comprises the step of feeding a gas fluid containing heat-expandable microspheres through a gas-introducing tube having a dispersion nozzle on its outlet and fixed inside a hot gas flow, and then jetting the gas flow from the dispersion nozzle, wherein each of the heat-expandable microspheres comprises a shell

of thermoplastic resin, a blowing agent encapsulated therein having a boiling point not higher than the softening point of the thermoplastic resin, and an average particle size from 1 to 100  $\mu\text{m}$ , and then colliding the gas fluid with a collision plate fixed on the lower portion of the dispersion nozzle to disperse the heat-expandable microspheres in the hot gas flow, and heating the dispersed  
5 heat-expandable microspheres in the hot gas flow at a temperature not lower than their expansion initiating temperature and thus expanding the heat-expandable microspheres.

[0024] The second production process for heat-expanded microspheres of the present invention comprises a step of jetting a gas fluid containing heat-expandable microspheres through at least one dispersion nozzle fixed outside a hot gas flow, and dispersing the gas fluid in the hot gas flow,  
10 wherein each of the heat-expandable microspheres comprises a shell of thermoplastic resin, and a blowing agent being encapsulated therein having a boiling point not higher than the softening point of the thermoplastic resin, and an average particle size from 1 to 100  $\mu\text{m}$ , and then heating the dispersed heat-expandable microspheres in the hot gas flow at a temperature not lower than their expansion initiating temperature to thereby expand the heat-expandable microspheres.

[0025] Heat-expanded microspheres of the present invention are produced in a process wherein heat-expandable microspheres, which comprise a shell of thermoplastic resin, and a blowing agent with a boiling point not higher than the softening point of the thermoplastic resin encapsulated in the shell, and have an average particle size ranging from 1 to 100  $\mu\text{m}$ , are heated and expanded at a temperature not lower than their expansion initiating temperature, and the heat-expanded  
20 microspheres contain not more than 5 weight percent of aggregated microspheres and not more than 5 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C.

[0026] Heat-expandable microspheres of the present invention comprise a shell of thermoplastic resin, and a blowing agent which has a boiling point not higher than the softening point of the thermoplastic resin and is encapsulated in the shell, have an average particle size ranging from 1 to 1000  $\mu\text{m}$  and an  
25 expansion coefficient above 100 %, and contain not more than 5 weight percent of aggregated microspheres and not more than 5 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C.

[0027] The porous material composition of the present invention contains a base component, and the heat-expanded microspheres and/or the heat-expandable microspheres.

30 The porous molded products of the present invention are produced by molding the porous material composition.

[0028] Other heat-expandable microspheres of the present invention comprise a shell of thermoplastic resin, and a blowing agent with a boiling point not higher than the softening point of the thermoplastic resin encapsulated in the shell, and have an average particle size ranging from 1 to 100  $\mu\text{m}$ . The  
35 blowing agent contains a  $\text{C}_{2-10}$  fluorine compound which has an ether structure, and does not contain chlorine and bromine atoms. The thermoplastic resin is produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group, the

monomer mixture in which the weight ratio of the nitrile monomer ranging from 20 to 80 weight percent, and the weight ratio of the monomer having a carboxyl group ranging from 80 to 20 weight percent.

[0029] Further, other heat-expandable microspheres of the present invention comprise a shell of thermoplastic resin, a blowing agent with a boiling point not higher than the softening point of the thermoplastic resin being encapsulated in the shell, and an anti-blocking agent adhered on the outer surface of the shell, and have an average particle size ranging from 1 to 100  $\mu\text{m}$ . The blowing agent contains a  $\text{C}_{2-10}$  fluorine compound which has an ether structure, and does not contain chlorine and bromine atoms. The thermoplastic resin is produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group, the monomer mixture in which the weight ratio of the nitrile monomer ranging from 20 to 80 weight percent, and the weight ratio of the monomer having a carboxyl group ranging from 80 to 20 weight percent. The anti-blocking agent comprises at least one substance selected from a group consisting of organic compounds having a melting point not lower than 90°C and inorganic compounds having a layered structure.

[0030] Further, other heat-expandable microspheres of the present invention comprise a shell of thermoplastic resin, a blowing agent with a boiling point not higher than the softening point of the thermoplastic resin being encapsulated in the shell, and an anti-blocking agent adhered on the outer surface of the shell, and have an average particle size ranging from 1 to 100  $\mu\text{m}$ . The blowing agent contains a  $\text{C}_{2-10}$  fluorine compound which has an ether structure, and does not contain chlorine and bromine atoms. The anti-blocking agent comprises at least one substance selected from a group consisting of organic compounds having a melting point not lower than 90°C and inorganic compounds having layered structure.

## Brief Description of the Drawings

[0031] FIG. 1 is a diagram of the expanding device of the production machine employed in the production process of the present invention.

FIG. 2 is a diagram of the expanding device of the production machine employed in another production process of the present invention.

## Description of Reference Numerals

[0032] 1 and 11: hot gas nozzle

2: cooling medium flow

3: overheat protection pipe

4 and 12: dispersion nozzle

5: collision plate

6 and 14: gas fluid containing heat-expandable microspheres

7: gas flow

8 and 13: hot gas flow

#### Best Mode for Carrying Out the Invention

##### 5 [0033] A. Production process for heat-expanded microspheres

###### a. Heat-expandable microspheres used as a starting material

In the first and second production processes for the heat-expanded microspheres of the present invention, the heat-expandable microspheres fed as a starting material (hereinafter sometimes referred to as “raw microspheres”) comprise a shell of thermoplastic resin, and a blowing agent which has a  
10 boiling point not higher than the softening point of the thermoplastic resin and is encapsulated in the shell, have an average particle size ranging from 1 to 100  $\mu\text{m}$ , and are not particularly limited.

[0034] The blowing agent encapsulated in a shell comprising a thermoplastic resin is a substance having a boiling point not higher than the softening point of the thermoplastic resin, and is not particularly limited. The examples of such blowing agents are  $\text{C}_{1-12}$  hydrocarbons and their halogen  
15 compounds, fluorine compounds, tetraalkyl silane and those which thermally decompose to generate gas, such as azodicarbonamide. At least one of those blowing agents is applied.

[0035] The examples of  $\text{C}_{1-12}$  hydrocarbons are propane, cyclopropane, propylene, butane, normal butane, isobutane, cyclobutane, normal pentane, cyclopentane, isopentane, neopentane, normal hexane, isohexane, cyclohexane, heptane, cycloheptane, octane, isooctane, cyclooctane, 2-methyl  
20 pentane, 2,2-dimethyl butane, and petroleum ether. Any of these hydrocarbons having a linear, branched or ali-cyclic structure are applicable, and aliphatic hydrocarbons are preferable.

The examples of halogen compounds of  $\text{C}_{1-12}$  hydrocarbons are methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. Halogen compounds (fluorine compounds, chlorine compounds, bromine compounds, iodine compounds, etc.) of the above-mentioned hydrocarbons are  
25 preferable.

[0036] Fluorine compounds are not particularly limited, but  $\text{C}_{2-10}$  compounds having an ether structure and containing no chlorine and bromine compounds are preferable. Examples of such compounds are hydrofluoroethers, such as  $\text{C}_3\text{H}_2\text{F}_7\text{OCF}_2\text{H}$ ,  $\text{C}_3\text{HF}_6\text{OCH}_3$ ,  $\text{C}_2\text{HF}_4\text{OC}_2\text{H}_2\text{F}_3$ ,  $\text{C}_2\text{H}_2\text{F}_3\text{OC}_2\text{H}_2\text{F}_3$ ,  $\text{C}_4\text{HF}_8\text{OCH}_3$ ,  $\text{C}_3\text{H}_2\text{F}_5\text{OC}_2\text{H}_3\text{F}_2$ ,  $\text{C}_3\text{HF}_6\text{OC}_2\text{H}_2\text{F}_3$ ,  $\text{C}_3\text{H}_3\text{F}_4\text{OCHF}_2$ ,  $\text{C}_3\text{HF}_6\text{OC}_3\text{H}_2\text{F}_5$ ,  $\text{C}_4\text{H}_3\text{F}_6\text{OCHF}_2$ ,  
30  $\text{C}_3\text{H}_3\text{F}_4\text{OC}_2\text{HF}_4$ ,  $\text{C}_3\text{HF}_6\text{OC}_3\text{H}_3\text{F}_4$ ,  $\text{C}_3\text{F}_7\text{OCH}_3$ ,  $\text{C}_4\text{F}_9\text{OCH}_3$ ,  $\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$ , and  $\text{C}_7\text{F}_{15}\text{OC}_2\text{H}_5$ . Those hydrofluoroethers may have either linear or branched (fluoro) alkyl groups.

[0037] The tetraalkyl silanes are those containing the same or different  $\text{C}_{1-5}$  alkyl groups. Examples of such compounds are tetraalkyl silanes, such as tetramethyl silane, trimethylethyl silane, trimethyl isopropyl silane, and trimethyl-n-propyl silane.

35 The compounds generating gas through thermal degradation are azodicarbonamide, N,N'-dinitroso pentamethylene tetramine, 4,4'-oxy bis (benzenesulfonyl hydrazide).

[0038] All of the blowing agent may comprise fluorine compounds, though compounds other than



fluorine compounds having a boiling point not higher than the softening point of the thermoplastic resin described below may be applied in combination with a fluorine compound. Such compounds are not particularly limited, and those selected from the examples of blowing agents described above can be applied. Compounds other than fluorine compounds can be selected according to the range of the expanding temperature of raw microspheres. In order to apply a fluorine compound as a blowing agent, the weight ratio of the fluorine compound is preferably greater than 50 weight percent of the whole of the blowing agent, more preferably greater than 80 weight percent, and most preferably greater than 95 weight percent. Greater weight ratio of a fluorine compound in a blowing agent is more advantageous in order to reflect more of the properties of the fluorine compound in the raw microspheres, and impart flame retardation and flameproof properties to the raw microspheres.

[0039] The raw microspheres comprise, for example, thermoplastic resin produced by polymerizing a monomer mixture containing a radically polymerizable monomer, and the shell of the raw material microspheres is formed by blending a proper amount of a polymerization initiator in the monomer mixture.

The examples of the radically polymerizable monomers, which are not particularly limited, are nitrile monomers, such as acrylonitrile, methacrylonitrile,  $\alpha$ -chloracrylonitrile,  $\alpha$ -ethoxyacrylonitrile, fumaronitrile; monomers having a carboxyl group, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid; vinylidene chloride; vinyl acetate; (meth)acrylate monomers, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, isobornyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, and  $\beta$ -carboxyethyl acrylate; acryl amide monomers, such as acryl amide, substituted acryl amide, methacrylamide, and substituted methacrylamide; and maleimide monomers, such as N-phenyl maleimide, N-(2-chlorophenyl) maleimide, N-cyclohexyl maleimide, and N-lauryl maleimide. One or a plurality of those radically polymerizable monomers are applicable.

[0040] A monomer mixture consisting essentially of a nitrile monomer is preferable for employing a blowing agent containing fluorine compounds, because such monomer mixture imparts heat resistance to thermoplastic resin. The preferable weight ratio of the nitrile monomer in the monomer mixture is 80 weight percent, more preferably 90 weight percent, and most preferably 95 weight percent, considering the heat resistance of the resultant thermoplastic resin.

[0041] A monomer mixture containing a nitrile monomer and a monomer having a carboxyl group is more preferable, because such monomer mixture imparts heat-resistance to raw microcapsules, and imparts a re-expanding capacity to heat-expanded microspheres produced by expanding raw microspheres and to re-expand heat-expanded microspheres at 90°C or higher temperature (preferably 100°C or higher and more preferably 120°C or higher), as described below. The preferable weight ratio of the nitrile monomer in a monomer mixture is 20 to 80 weight percent, more preferably 20 to 60 weight percent, further preferably 20 to 50 weight percent, and most preferably 20 to 40 weight percent, considering the retention of a blowing agent encapsulated in microspheres, its blowing

performance, the control over the re-expansion initiating temperature of heat-expanded microspheres, and the evaluation of high-speed running performance with normal internal pressure described below. The preferable weight ratio of the monomer having a carboxyl group in a monomer mixture is 20 to 80 weight percent, more preferably 40 to 80 weight percent, further preferably 50 to 80 weight percent, and most preferably 60 to 80 weight percent, considering the control over the re-expansion initiating temperature of heat-expanded microspheres, the evaluation of high-speed running performance with normal internal pressure described below, the retention of a blowing agent encapsulated in microspheres, and its blowing performance.

[0042] The monomer mixture may contain a polymerizable monomer having at least two polymerizable double bonds (a cross-linking agent) in addition to the radically polymerizable monomers. Polymerization with a cross-linking agent contributes to a reduced ratio of aggregated microspheres in heat-expanded microspheres produced by the production process of the present invention, minimum reduction of the retention of encapsulated blowing agent in microspheres after heat-expansion (retention of encapsulated blowing agent), and efficient heat-expansion of microspheres.

The retention (%) of encapsulated blowing agent in microspheres after heat-expansion in the present invention is defined as  $G_2/G_1 \times 100$ , where  $G_1$  is the retention of a blowing agent encapsulated in raw material microspheres before expansion, and  $G_2$  is the retention of blowing agent encapsulated in heat-expanded microspheres produced by heating and expanding.

[0043] The examples of cross-linking agents, but not limited to these examples, are aromatic divinyl compounds, such as divinyl benzene and divinyl naphthalene; and di(meth)acrylates, such as allyl methacrylate, triacrylformal, triallyl isocyanate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, PEG (200) di(meth)acrylate, PEG (400) di(meth)acrylate, PEG (600) di(meth)acrylate, neopentylglycol di(meth)acrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, trimethylolpropane trimethacrylate, glycerin dimethacrylate, dimethylol tricyclodecane diacrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, neopentylglycol acrylic acid benzoate, trimethylolpropane acrylic acid benzoate, 2-hydroxy-3-acryloyloxypropyl methacrylate, hydroxyphthalic acid neopentylglycol diacrylate, ditrimethylolpropane tetraacrylate, and 2-butyl-2-ethyl-1,3-propanediol diacrylate. One of or a plurality of those cross-linking agents are applicable.

[0044] The preferable weight ratio of the cross-linking agents is 0.01 to 5 weight percent of the monomer mixture, more preferably 0.05 to 3 weight percent, considering the degree of cross-linking, the retention of the blowing agent encapsulated in the shell, and the heat-resistance and heat-expansion of the microspheres, though the weight ratio is not restricted within those ranges.

[0045] The polymerization initiator is not particularly limited, and known polymerization initiators

can be applied. The examples of those polymerization initiators are peroxides, such as t-butyl peroxy isobutylate, t-butyl peroxy-2-ethyl hexanoate, t-hexyl peroxy-2-ethyl hexanoate, 2,5-dimethyl-2,5-bis(2-ethyl hexanoyl peroxy) hexane, 1,1,3,3-tetramethylbutyl peroxy-2-ethyl hexanoate, t-butyl peroxy pivalate, t-hexyl peroxy pivalate, t-butyl peroxy neodecanoate, t-hexyl peroxy neodecanoate, 1-cyclohexyl-1-methylethyl peroxy neodecanoate, 1,1,3,3-tetramethylbutyl peroxy neodecanoate, cumyl peroxy neodecanoate, di-n-propyl peroxy dicarbonate, diisopropyl peroxy dicarbonate, bis(4-t-butylcyclohexyl) peroxy dicarbonate, di-sec-butyl peroxy dicarbonate, di-2-ethoxyethyl peroxy dicarbonate, di-2-ethylhexyl peroxy dicarbonate, di-3-methoxybutyl peroxy dicarbonate 3,5,5-trimethyl hexanoyl peroxide, octanoyl peroxide, lauroyl peroxide, stearyl peroxide, succinic acid peroxide, and benzoyl peroxide; and azo compounds, such as 2,2'-azobis (4-methoxy-2,4-dimethyl valeronitrile), 2,2'-azobis isobutyronitrile, 2,2'-azobis (2,4-dimethyl valeronitrile), 2,2'-azobis (2-methyl propionate), and 2,2'-azobis (2-methyl butyronitrile). Preferable polymerization initiators are oil-soluble polymerization initiators which are soluble in radically polymerizable monomers.

[0046] The raw microspheres are produced in conventionally known processes for producing heat-expandable microcapsules.

Those processes include suspension polymerization wherein a mixture of radically polymerizable monomers, a cross-linking agent as an option, and a polymerization initiator is mixed with a blowing agent, and the resultant mixture is suspension polymerized in an aqueous medium containing a proper dispersion stabilizer.

[0047] The examples of the dispersion stabilizers in the aqueous suspension are colloidal silica, colloidal calcium carbonate, magnesium hydroxide, calcium phosphate, aluminum hydroxide, ferric hydroxide, calcium sulfate, sodium sulfate, calcium oxalate, calcium carbonate, barium carbonate, magnesium carbonate, and alumina sol. The preferable ratio of the dispersion stabilizer in the monomer mixture is 0.1 to 20 weight percent. As dispersion-stabilizing auxiliaries polymer-type such as diethanol amine-aliphatic dicarboxylic acid condensates, gelatine, polyvinyl pyrrolidone, methyl cellulose, polyethylene oxide and polyvinyl alcohol; and emulsifiers including cationic surfactants such as alkyltrimethyl ammonium chloride and dialkyldimethyl ammonium chloride, anionic surfactants such as sodium alkyl sulfate, and amphoteric surfactants such as alkyldimethyl betaine aminoacetate and alkyldihydroxyethyl betaine aminoacetate may be applied. The preferable ratio of the dispersion-stabilizing auxiliary is 0.05 to 2 weight percent of the monomer mixture.

[0048] An aqueous suspension containing a dispersion stabilizer is prepared by mixing a dispersion stabilizer and an auxiliary for the dispersion stabilizer in water (for example, deionized water). The pH of the aqueous suspension during polymerization is properly determined according to the variants of a dispersion stabilizer and an auxiliary for the dispersion stabilizer. A water-soluble reducing agent may be added to the aqueous suspension, and it suppresses the formation of aggregated microspheres during polymerization. The examples of the water-soluble reducing agents are nitrites

of alkali metals, such as sodium nitrite and potassium nitrite, stannous chloride, stannic chloride, ferrous chloride, ferric chloride, ferrous sulfate, and water-soluble ascorbic acids. Among those, nitrites of alkali metals are preferable considering their stability in water. The preferable ratio of the reducing agents is 0.0001 to 1 weight percent of the monomer mixture, more preferably 0.0003 to 0.1 weight percent.

[0049] The polymerization temperature is controlled according to the variants of polymerization initiators, preferably ranging from 40 to 100°C, more preferably from 45 to 90°C, and most preferably from 50 to 85°C. The initial pressure for the polymerization ranges from 0 to 5.0 MPa in gage pressure, preferably from 0.1 to 3.0 MPa, and more preferably from 0.2 to 2.0 MPa.

[0050] The ratio of the blowing agent in the resultant raw microspheres is controlled from 2 to 85 weight percent of the raw microspheres, more preferably from 5 to 60 weight percent, and most preferably from 7 to 50 weight percent, from the view point of attaining superior blowing performance which enables expanded microspheres to function satisfactorily as an internal pressure supplier for tires when filled in a tire-and-rim assembly, and of achieving sufficient thickness of the thermoplastic resin shell of the heat-expandable microspheres in order to maintain the retention of encapsulated blowing agent. The preferable ratio of a blowing agent containing fluorine compounds is 10 to 60 weight percent, more preferably 15 to 50 weight percent.

[0051] The average particle size of raw microspheres may be freely designed according to their application, and therefore is not particularly limited. For encapsulating a blowing agent containing fluorine compounds, a preferable average particle size ranges is from 1 to 100 µm, more preferably 2 to 80 µm, and most preferably 5 to 60 µm.

The coefficient of variation, CV, of the particle size distribution of the raw microspheres is not particularly limited, but is preferably 30 % or less, more preferably 27 % or less, and most preferably 25 % or less. The coefficient of variation, CV, is calculated from the following expressions (1) and (2).

[0052] [Expression 1]

$$CV = (s / \langle x \rangle) \times 100 (\%) \quad \dots\dots\dots(1)$$

$$s = \left\{ \sum_{i=1}^n (x_i - \langle x \rangle)^2 / (n - 1) \right\}^{1/2} \quad \dots\dots\dots(2)$$

Where s is a standard deviation of particle size,  $\langle x \rangle$  is an average particle size,  $x_i$  is a particle size of an i-th greatest particle, and n is the number of particles.

[0053] Adhering a particulate filler on the outer surface of the shell of raw microspheres is preferable for improving their dispersibility and flowability.

A particulate filler may be an organic or inorganic filler, and the variants and amount of

particulate fillers are selected according to the purpose of their application.

[0054] The examples of organic fillers are metal soaps, such as magnesium stearate, calcium stearate, zinc stearate, barium stearate, and lithium stearate; synthetic waxes, such as polyethylene wax, lauric acid amide, myristic acid amide, palmitic acid amide, stearic acid amide, and hydrogenated castor oil; and resin powders, such as polyacryl amide, polyimide, nylon, methyl polymethacrylate, polyethylene, and polytetrafluoroethylene.

[0055] The examples of inorganic fillers are those having a layered structure, such as talc, mica, bentonite, sericite, carbon black, molybdenum disulfide, tungsten disulfide, carbon fluoride, calcium fluoride, and boron nitride; and others, such as silica, alumina, isinglass, calcium carbonate, calcium hydroxide, calcium phosphate, magnesium hydroxide, magnesium phosphate, barium sulfate, titanium dioxide, zinc oxide, ceramic beads, and crystal beads.

One of or a plurality of those particulate fillers may be applied.

[0056] A preferable particulate filler for adhering on the outer surface of the shell of microspheres is one selected from organic compounds having a melting point not lower than 90°C (or not lower than 100°C, preferably not lower than 110°C, more preferably not lower than 120°C, further preferably not lower than 150°C, and most preferably not lower than 200°C), or one selected from inorganic compounds having a layered structure (preferably at least one selected from the group consisting of carbon black, molybdenum disulfide, tungsten disulfide, carbon fluoride, and boron nitride), in other words, an anti-blocking agent. The anti-blocking agent prevents the fusion of the resin forming the shell of the raw microspheres and/or heat-expanded microspheres, and further prevents the fusion of adjacent raw microspheres and/or heat-expanded microspheres in heating and expanding, and has a function which will not deteriorate the expanding performance of microspheres. Such performance of the anti-blocking agent enables heat-expanded microspheres, which are produced by expanding raw material microspheres and have re-expanding capacity, to immediately seal damage on tires and to supply internal pressure to damaged tires that have lost their internal pressure, when the heat-expanded microspheres are filled in a tire-and-rim assembly, and thus makes damaged tires runnable to a required distance as described below. A blowing agent containing fluorine compounds remarkably develops such effect.

[0057] Raw microspheres comprising a shell of thermoplastic resin produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group exhibit superior heat-resistance and flame-retardation (flameproof properties), and are processed into heat-expanded microspheres having the ability to re-expand at 90°C or higher temperature (preferably at 100°C or higher, and more preferably at 120°C or higher), and exhibit the above-mentioned effects remarkably.

[0058] The average particle size of a particulate filler is preferably not greater than one tenth of the average particle size of the raw microspheres before adhering the particulate filler. The average particle size means an average particle size of the primary particles.

[0059] The amount of a particulate filler adhered on the raw microspheres is not particularly limited, and is preferably 0.1 to 95 weight percent of raw microspheres before adhering the filler, more preferably 0.5 to 60 weight percent, further preferably 5 to 50 weight percent, and most preferably 8 to 30 weight percent, considering the true specific gravity of heat-expandable microspheres and the optimization of the function of a particulate filler.

[0060] A particulate filler is adhered on the outer surface of raw microspheres by mixing raw microspheres and a particulate filler. The mixing process is not particularly limited, and a device equipped with simple tools, such as a vessel and paddle blades is employable. Ordinary powder mixers for shaking or agitating powders are also applicable. The examples of powder mixers are those which can shake and agitate, or agitate powders, such as ribbon-type mixers and vertical screw mixers. Recently, highly efficient multi-functional powder mixers manufactured by combining several agitation devices, such as Super Mixer (manufactured by Kawata MFG Co., Ltd.), High-Speed Mixer (manufactured by Fukae Co., Ltd.) and New-Gram Machine (manufactured by Seishin Enterprise Co., Ltd.), have become available.

[0061] Raw microspheres are applicable as a volume retention material, for example, by filling them in a tire-and-rim assembly and expanding with heating at a temperature not lower than the expansion initiating temperature of the raw material microspheres. In addition, raw microspheres may be applied as a lightweight filler for automobile paints, expanding particles in expandable inks for wall paper and apparel design, and an expanding material for lightening resin compositions.

[0062] b. Production process for heat-expanded microspheres

The first production process for the heat-expanded microspheres of the present invention comprises the step of feeding a gas fluid containing heat-expandable microspheres through a gas-introducing tube having a dispersion nozzle on its outlet and fixed inside a hot gas flow, and then jetting the gas flow from the dispersion nozzle (jetting step), wherein each of the heat-expandable microspheres comprises a shell of thermoplastic resin and a blowing agent encapsulated therein and has a boiling point not higher than the softening point of the thermoplastic resin and have an average particle size from 1 to 100  $\mu\text{m}$ , colliding the gas fluid on a collision plate fixed on a lower portion of the dispersion nozzle to disperse heat-expandable microspheres in the hot gas flow (dispersing step), and heating the dispersed heat-expandable microspheres in the hot gas flow at a temperature not lower than their expansion initiating temperature and thus expanding the heat-expandable microspheres (expanding step).

[0063] The production process is operated with production machines, for example, the machine having an expanding device as illustrated in Figure 1.

The expanding device comprises a gas-introducing tube (not marked with a number) being equipped with a dispersion nozzle 4 on its outlet and fixed at the center of the device; a collision plate 5 fixed on a lower portion of the dispersion nozzle 4; a over-heating protection pipe 3 fixed around the gas-introducing tube at a proper distance; and a hot gas nozzle 1 fixed around the over-heating

protection pipe 3 at a proper distance. At the expanding device, the gas fluid containing heat-expandable microspheres 6 runs through the gas-introducing tube in the direction shown with the arrow, and the gas flow 7 runs through the space between the gas-introducing tube and over-heating protection pipe 3 in the direction shown with the arrow, to improve the dispersion of heat-expandable microspheres and to protect the gas-introducing tube and the collision plate from excessive heating. Further, the hot gas flow 8 for heating and expanding runs through the space between the over-heating protection pipe 3 and the hot gas nozzle 1 in the direction shown with the arrow. The hot gas flow 8, gas fluid 6, and gas flow 7 do not necessarily flow in the same direction, though they usually flow in the same direction. In the over-heating protection pipe 3, the cooling medium 2 for cooling is made to flow in the direction shown with the arrow.

The gas-introducing tube and/or the collision plate 5 having the over-heating protection system is preferable for controlling the generation of aggregated or fused microspheres.

The shape of the collision plate is not particularly limited, and its form may be spindle-like, conical, pyramidal, spherical, or semi-spherical form, and a combination of those forms.

[0064] At the jetting step of the first production process, the gas fluid containing heat-expandable microspheres 6 is made to flow into the gas-introducing tube equipped with the dispersion nozzle 4 on its outlet and fixed inside the hot gas flow 8, and is jetted from the dispersion nozzle 4. The gas fluid containing heat-expandable microspheres 6 is not particularly limited, so long as it is a gas containing heat-expandable microspheres. Preferable gas fluids are those comprising inert gases, such as air, nitrogen, argon, and helium containing heat-expandable microspheres.

The moisture in the gas fluid 6 is preferably not more than  $30 \text{ g/m}^3$ , more preferably not more than  $9.3 \text{ g/m}^3$ , in order to prevent poor dispersion of heat-expandable microspheres.

The flow rate of the gas fluid 6 is preferably controlled at a rate at which each heat-expandable microsphere is subjected to the same heat history as far as possible, in order to be expanded in the subsequent dispersing step, though the rate is not particularly limited.

[0065] At the dispersing step of the first production process, the gas fluid 6 is collided with the collision plate 5 fixed under the dispersion nozzle 4 for dispersing heat-expandable microspheres uniformly in the hot gas flow 8. The gas fluid 6 coming out of the dispersion nozzle 4 is introduced to the collision plate 5 with the gas flow 7 and is collided with the plate.

The same gas as that for the gas fluid 6 is applicable for the gas flow 7.

[0066] At the expanding step of the first production process, dispersed heat-expandable microspheres are heated and expanded in the hot gas flow, 8, at a temperature not lower than the expansion initiating temperature of the microspheres. Then the heat-expanded microspheres are cooled down below the softening point of the thermoplastic resin forming the shell of the heat-expandable microspheres by feeding the heat-expanded microspheres through a cooling zone or with other measures, and the heat-expanded microspheres are collected.

Ordinary solid-gas separators, such as cyclone separators or bag filters, are preferable for the

collection.

[0067] The second production process for the heat-expanded microspheres of the present invention comprises a step of jetting a gas fluid containing heat-expandable microspheres through at least one dispersion nozzle fixed outside hot gas flow (dispersing step), and dispersing the gas fluid in the hot gas flow, wherein each of the heat-expandable microspheres comprises a shell of thermoplastic resin and a blowing agent being encapsulated therein and having a boiling point not higher than the softening point of the thermoplastic resin and have an average particle size from 1 to 100  $\mu\text{m}$ , and heating the dispersed heat-expandable microspheres in the hot gas flow at a temperature not lower than their expansion initiating temperature and thus expanding the heat-expandable microspheres (expanding step).

[0068] The production process is operated with production machines, for example, the machine having the expanding device as illustrated in Figure 2.

The expanding device comprises the hot gas nozzle 11 fixed at the center of the device, and at least one dispersion nozzle 12 fixed around the bottom of the hot gas nozzle. At the expanding step, the hot gas flow 13 for expanding microspheres is fed through the hot gas nozzle 11 in the direction shown with the arrow, and the gas fluid containing heat-expandable microspheres 14 is fed through the dispersion nozzle 12 in the direction shown with the arrow. The gas fluid 14 may be fed almost orthogonally to the direction of the hot gas flow 13, though the direction of the gas fluid is usually slanted downward so as to not to feed the gas fluid orthogonally to the hot gas flow.

[0069] At the dispersing step of the second production process, the gas fluid containing heat-expandable microspheres 14 is jetted from at least one dispersion nozzle 12 fixed outside the hot gas flow 13, and heat-expandable microspheres are dispersed into the hot gas flow. The gas fluid 14 is the same as the gas fluid 6 mentioned above. The moisture content and flow rate of the gas fluid 14 may be controlled into the same as those of the gas fluid 6 mentioned above.

[0070] At the expanding step of the second production process, dispersed heat-expandable microspheres are heated and expanded in the hot gas flow 13 at a temperature not lower than the expansion initiating temperature of the microspheres. Then the heat-expanded microspheres are collected in the same manner as those of the first production process.

[0071] Adding a step for wetting heat-expanded microspheres with a liquid organic compound (wetting step) after the expanding step in the first and second production processes is preferable, because it prevents dust formation from heat-expanded microspheres and improves the dispersibility of heat-expanded microspheres in a mixing process in their application. Preferable liquid organic compounds may basically have the properties (1) and (2) described below, and may be selected according to the properties of the produced heat-expanded microspheres and the aim of their application, though the liquid organic compound is not particularly limited:

(1) a boiling point higher than the gasifying point of a blowing agent encapsulated in heat-expanded microspheres



(2) a wetting function that will not dissolve and swell thermoplastic resin which forms the shell of the heat-expanded microspheres

[0072] The boiling point of the liquid organic compound ranges preferably from 80 to 270°C, more preferably from 90 to 260°C, and most preferably from 100 to 250°C, in order to meet the above requirement (1) and avoiding vaporization during storage.

Raw microspheres produced with the cross-linking agent described above contribute to improved solvent resistance of heat-expanded microspheres produced in the production process of the present invention. Such improved solvent resistance meets the above requirement (2) to expand the scope of the liquid organic compounds considerably.

[0073] The variants of the liquid organic compounds are not particularly limited. The examples of the liquid organic compounds are plasticizers, such as dibutyl phthalate, diisooctyl phthalate, dioctyl adipate, tricresyl phosphate, triethyl citrate, acetyltributyl citrate, and octyl alcohol, for applying resultant wet composition to plastics, elastomers, sealants, and paints; and monomers, such as dicyclopentane and styrene, for applying resultant wet composition to lightweight molded expanded products and adhesives. The examples of liquid organic compounds other than those mentioned above are nonionic surfactants, alkylene glycol, polyalkylene glycol, glycerin, silicone oil, liquid paraffin, and oils and fats. Two or more of those liquid organic compounds may be blended to be applied, and water is applicable instead of those liquid organic compounds.

[0074] The ratio between heat-expanded microspheres and a liquid organic compound (or water) is not particularly limited, and may be determined according to the surface property of heat-expanded microspheres and the extent of generated dust due to the true specific gravity of heat-expanded microspheres. Specifically, preferable ratios are those which decrease dust generation from heat-expanded microspheres to an indistinctive level. An excessive ratio of a liquid organic compound results in unevenly mixed liquid organic compound and heat-expanded microspheres due to excessive liquid organic compound in the mixture. For avoiding such mixture, the preferable ratio of a liquid organic compound is, for example, 90 parts by weight or less to 10 parts by weight of heat-expanded microspheres having a true specific gravity of 0.03 g/cc. On the other hand, insufficient ratio of a liquid organic compound is not preferable, because it leads to the generation of dust to a noticeable level.

[0075] At the wetting step, heat-expanded microspheres are shaken or agitated with a liquid organic compound. The shaking and agitating are performed with ordinary powder mixers, for example, mixers applicable to mixing heat-expandable microspheres and a particulate filler, and in addition operated with a dual-rotor mixer.

[0076] The wetting step is further described in detail, although the step is not restricted within the scope of the description. A predetermined amount of heat-expanded microspheres is placed in a device employed for the wetting step (hereinafter referred as wetting device), and a liquid organic compound (or water) is added. The liquid organic compound is discharged from one opening per

0.07 m<sup>2</sup> or wider area of the surface of heat-expanded microspheres to be shaken or agitated (for example, a flow rate not faster than 2 liters/min), and then the heat-expanded microspheres are shaken or agitated in the device until they are wet uniformly. The opening is fixed over the surface of microspheres or in the microspheres to be shaken or agitated. The area of the surface of microcapsules to be shaken or agitated per one opening should be controlled to make the liquid organic compound contact well with microspheres and to attain uniform wetting of whole of the microspheres, not to inhibit the movement of shaken or agitated heat-expanded microspheres due to the interference effect of a liquid organic compound discharged from a plurality of openings. The discharge rate of the liquid organic compound should be controlled in order to make it contact well with the shaken or agitated microspheres and to attain uniform wetting of all of the microspheres.

[0077] A movable opening which can move over the surface or inside of shaken or agitated microspheres is highly efficient, though the efficiency depends on its moving speed. For example, an opening movable at a rate of 20 cm/sec can discharge a liquid organic compound about 5 times of that discharged from a fixed opening, and shorten the shaking or agitating time required for uniform wetting after adding a liquid organic compound.

[0078] The opening may be simply an end of pipe or hose. Shower heads or spray nozzles may also be employed. A viscous liquid organic compound discharged with pressure and flowed into microspheres in cylindrical form does not scatter a lot of microspheres. A liquid sprayed with excessively high pressure scatters microspheres that are being shaken or agitated, and it requires the sealing of a wetting device or a dust collector.

[0079] After adding a liquid organic compound to heat-expanded microspheres, the microspheres are shaken or agitated until they are uniformly wet. The endpoint of the wetting is determined by picking up samples from a plurality of points in the wetting device, determining the true specific gravity of each 0.5 to 0.8 g of the samples with a liquid substitution method, and checking the deviation, for example, the standard deviation, of the values.

In the first or second production process, the preferable moisture content in heat-expandable microspheres is 5 % or less, more preferably 3 % or less, in order to attain uniform heating and expanding of the microspheres.

[0080] In the first or second production process, the expansion conditions can be controlled to produce heat-expanded microspheres having or not having a re-expansion initiating temperature. In the present invention, microspheres having a re-expansion initiating temperature are the same as the heat-expanded microspheres which have the capacity to re-expand with heating. The temperature at which the heat-expanded microspheres start to re-expand is referred as a re-expansion initiating temperature. Heat-expanded microspheres having a re-expansion initiating temperature are equal to the heat-expanded microspheres having an expansion coefficient greater than 100 % at their maximum (re-)expanding temperature. On the other hand, microspheres having no re-expansion initiating temperature are equivalent to almost completely heat-expanded microspheres.

[0081] The expansion conditions are not particularly limited. For example, at first, microspheres are expanded with varied temperature levels of hot gas flow (hereinafter sometimes referred as “hot gas temperature”), while other conditions, such as the feeding rate of raw material, the flow rate of hot gas, and the amount of gas for dispersing raw material, are controlled to be constant. Then, the true specific gravity of expanded microspheres processed at each hot gas temperature level with other parameters controlled to be constant is determined. The hot gas temperature (x-axis) and true specific gravity (y-axis) are plotted and drawn into a graph. Heat-expandable microspheres having no re-expansion initiating temperature can be produced by controlling the hot gas temperature within the temperature range on the graph corresponding to the minimum true specific gravity of expanded microspheres (the minimum value in the graph).

For producing expanded microspheres having a prescribed true specific gravity, the hot gas temperature is controlled at the temperature corresponding to the required true specific gravity on the graph. Thus, the expansion conditions are controlled in order to produce heat-expanded microspheres having a prescribed re-expanding capacity.

In order to change the feeding rate of the raw material and/or the gas for dispersing the raw material, the hot gas temperature and other parameters are changed so as to control the expansion conditions, based on the consideration of the amount of heat supplied with the hot gas flow and the entire heat capacity of the raw material microspheres, and the heat-expandable microspheres. For example, the hot gas temperature is increased in order to increase the feeding rate of raw material and the gas for dispersing the raw material. In order to decrease the feeding rate of the raw material and the gas for dispersing the raw material, the hot gas temperature is decreased.

[0082] In the first or second production processes, microspheres can be dispersed well and applied almost the same heat history to each of raw microspheres continuously owing to their high energy efficiency and easy temperature control. Thus, the difference in the coefficient of variation of particle size distribution of the microspheres before and after expansion is small, and the resultant heat-expanded microspheres have uniform qualities (especially particle size distribution and the distribution of true specific gravity). In other words, aggregated microspheres in the resultant heat-expanded microspheres are minimized, and the ratio of raw material and slightly expanded microspheres is also minimized.

[0083] The resultant heat-expanded microspheres are applied as a sealant for damaged tires, and/or an internal pressure supplier for damaged tires that have lost their internal pressure, by filling the same into a tire-and-rim assembly.

The sealant for damaged tires mentioned here means a sealant which can instantaneously seal the damaged portion of a tire with raw microspheres or heat-expanded microspheres that are transferred with a filled gas fluid so as to aggregate at the damaged portion when a tire is damaged and filled gas starts to leak through the damaged portion thereof. The internal pressure supplier is that which can increase the internal pressure of a damaged tire after the damage has been sealed with

a sealant for damaged tires. Raw material microspheres or heat-expanded microspheres are rubbed together in the damaged tire, in which the volume of filled gas has decreased due to the deformation of the tire as a result of decreased internal pressure, and the temperature in the tire increases to the expansion initiating temperature of the microspheres so as to expand the microspheres, which subsequently function to increase the internal pressure of the damaged tire.

[0084] The temperature of heat-expanded microspheres filled in tires sometimes rises due to the contact between the microspheres or between the microspheres and the internal rubber surface of a tire, which is caused from the rotating motion of tires during driving of automobiles. If the temperature of heat-expanded microspheres rises above their expansion initiating temperature in running tires without damage, heat-expanded microspheres start to expand and may lose their performance for supplying internal pressure to damaged tires. In addition, the risk of losing the internal-pressure-supplying performance for damaged tires is higher in high-speed driving than in normal speed driving.

The heat-expanded microspheres produced in the production process of the present invention show satisfactory result when they are filled in tires and evaluated their running performance in high-speed driving with normal pressure and in high-speed driving with normal pressure as described below.

[0085] B. Heat-expanded microspheres

The heat-expanded microspheres of the present invention are those produced in the production process wherein heat-expandable microspheres comprising a shell of thermoplastic resin and a blowing agent with a boiling point not higher than the softening point of the thermoplastic resin being encapsulated in the shell, and having an average particle size ranging from 1 to 100  $\mu\text{m}$  are heated at their expansion initiating temperature or higher temperature. The raw heat-expandable microspheres mentioned here are preferably, but not being particularly limited, the heat-expandable microspheres described in the above "A. Production process of heat-expanded microspheres". The production process for heating and expanding heat-expandable microspheres at their expansion initiating temperature or higher temperature is preferably, but not particularly limited, the production process described in the above "A. Production process of heat-expanded microspheres".

[0086] The average particle size of heat-expanded microspheres is not particularly limited, and may be freely designed according to their application. For example, considering the retention of a blowing agent in shell and the durability of heat-expanded microspheres, a preferable average particle size ranges from 1 to 1000  $\mu\text{m}$ , more preferably 5 to 800  $\mu\text{m}$ , and most preferably 10 to 500  $\mu\text{m}$ .

[0087] The ratio of aggregated microspheres in heat-expanded microspheres is preferably not higher than 5 weight percent, more preferably not more than 1 weight percent, further preferably not more than 0.5 weight percent, and most preferably not more than 0.3 weight percent, considering the uniformity of their true specific gravity. Aggregated microspheres are identified by visual inspection through electron microscope, and their quantity can be determined by measuring the residue from

screening as precisely described in the examples below.

[0088] The ratio of microspheres having a true specific gravity not lower than 0.79 g/cc contained in heat-expanded microspheres at 25°C is preferably not higher than 5 weight percent, more preferably not higher than 3 weight percent, further preferably not higher than 2 weight percent, and most preferably not higher than 1 weight percent, considering the uniformity of their true specific gravity. The ratio of microspheres having a true specific gravity not lower than 0.79 g/cc is determined by quantitative analysis of the precipitation remained after the separation by specific gravity with isopropyl alcohol (having a specific gravity of 0.79 at 25°C).

[0089] The coefficient of variation, CV, of the particle size distribution of heat-expanded microspheres should not be much different from the CV of the particle size distribution of raw heat-expandable microspheres for maintaining the uniformity of particle size, and thus the difference in the CV of the particle size distribution of microspheres before and after heat-expansion is preferably within +/-10 %, more preferably within +/-5 %, further preferably within +/-3 %, and most preferably within +/-1 %. The difference in the coefficient of variation, CV, is defined as the difference obtained by subtracting the coefficient of variation of the particle size distribution of raw material heat-expandable microspheres from the coefficient of variation of the particle size distribution of resultant heat-expanded microspheres. The preferable coefficient of variation of the particle size distribution of heat-expanded microspheres is 30 % or smaller, more preferably 27 % or smaller, and most preferably 25 % or smaller.

[0090] The heat-expanded microspheres of the present invention contain slight ratios of aggregated microspheres and microspheres having high true specific gravity, and the coefficient of variation in their particle size distribution is not much different from the coefficient of variation of their particle size distribution before heat-expansion.

[0091] The heat-expanded microspheres of the present invention may have or may not have a re-expansion initiating temperature.

The heat-expanded microspheres having a re-expansion initiating temperature have comparatively thick shell of thermoplastic resin, and are durable against external force. Such microspheres collapse minimally in mixing with a base component for producing porous material composition containing heat-expanded microspheres. In addition, such microspheres prevent porous molded products containing heat-expanded microspheres from time-dependent thermal deflation or hardening and shrinking. Heat-expanded microspheres having a re-expansion initiating temperature preferably have the property of the heat-expandable microspheres A described below.

[0092] The expansion coefficient of the heat-expanded microspheres of the present invention, in other words, the ratio of the volume of heat-expanded microspheres to their volume before heat-expanding, is not particularly limited, but preferably not smaller than 8 times, more preferably not smaller than 15 times, and most preferably not smaller than 30 times. The true specific gravity of heat-expanded microspheres is preferably, but not particularly limited, not greater than 0.30 g/cc, more preferably not

greater than 0.25 g/cc, and most preferably not greater than 0.20 g/cc. The “true specific gravity” of heat-expanded microspheres in this specification means their “mean true specific gravity”.

[0093] The retention of a blowing agent in the heat-expanded microspheres of the present invention is not particularly limited, but preferably not lower than 80 %, more preferably not lower than 85 %, and most preferably not lower than 90 %, considering the amount of leaked blowing agent through shell, uniformity of their performance, and their stability.

For applying a fluorine compound as a blowing agent, the preferable retention is not lower than 90 %, more preferably not lower than 95 %, and most preferably not lower than 97 %.

[0094] Keeping the heat-expanded microcapsules of the present invention in wet state with a liquid organic compound, which does not dissolve their shell, is preferable, because it prevents dust generation from the microspheres and improves the dispersibility of the microspheres in mixing for various applications. The variants and ratio of the liquid organic compound may be similar to those described in “A. Production process for heat-expanded microspheres.

[0095] A preferable blowing agent encapsulated in heat-expanded microspheres is, in particular, one containing a C<sub>2-10</sub> fluorine compound having ether structure and no chlorine or bromine atoms, as precisely described in “A. Production process for heat-expanded microspheres. Such blowing agent enables resultant heat-expanded microspheres being filled in a tire-and-rim assembly to exhibit superior performance for sealing damage on a tire and supplying internal pressure to a tire, when a tire is damaged to lose its internal pressure. In addition, such blowing agent brings satisfactory result in the evaluation of tire running performance with a normal internal pressure and high-speed tire running performance with a normal internal pressure. Further, such blowing agent enables to control the re-expansion initiating temperature of heat-expanded microspheres into a temperature preferably not lower than 90°C, more preferably not lower than 100°C, further preferably not lower than 110°C, and most preferably not lower than 120°C, and heat-expanded microcapsules having such re-expansion initiating temperature can be applied as a sealant for damage on tires and/or an internal pressure supplier for tires without restriction from the environment where tires are used.

[0096] The heat-expanded microspheres of the present invention may be applied as lightweight fillers for putty, paints, sealants, mortars, papier-mâché, and pottery, though such application is not particularly limited.

#### [0097] C. Heat-expandable microspheres A

The heat-expandable microspheres of the present invention (hereinafter sometimes referred to as “heat-expandable microspheres A”) are novel heat-expanding microspheres comprising a shell of thermoplastic resin and a blowing agent being encapsulated in the shell and having a boiling point not higher than the softening point of the thermoplastic resin, and having the following properties (I) to (IV).

(I) an average particle size ranging from 1 to 1000 μm

(II) an expansion coefficient over 100 % at a maximum expanding temperature

(III) a ratio of aggregated microspheres not higher than 5 weight percent

(IV) a ratio of microspheres having a true specific gravity not smaller than 0.79 g/cc at 25°C not higher than 5 weight percent

[0098] The heat-expandable microspheres A are produced by heating and expanding raw material microspheres to retain a capacity of re-expanding (in other words, to have a re-expansion initiating temperature) as in “A. Production process for heat-expanded microspheres”. The expansion coefficient of the heat-expandable microspheres A is between the expansion coefficient of raw material microspheres at their maximum expanding temperature and the expansion coefficient of almost completely heat-expanded microspheres at their maximum expanding temperature. The same order would apply to their average particle sizes and true specific gravities.

[0099] The average particle size of the heat-expandable microspheres A is preferably 1 to 1000  $\mu\text{m}$ , more preferably 5 to 800  $\mu\text{m}$ , further preferably 10 to 500  $\mu\text{m}$ , and most preferably 15 to 350  $\mu\text{m}$ , considering the retention of a blowing agent in shell, degree of re-expanding, and durability of heat-expanded microspheres.

[0100] The expansion coefficient of the heat-expandable microspheres A at their maximum expanding temperature is over 100 %, preferably over 105 %, more preferably over 120 %, further preferably over 130 %, and most preferably over 150 %, intending to produce heat-expandable microspheres without losing heat-expanding performance. The fact that the heat-expandable microspheres A have an expansion coefficient over 100 % means almost the same fact that the heat-expandable microspheres A have an expansion initiating temperature, as described above.

[0101] The ratio of aggregated microspheres contained in the heat-expandable microspheres A should be not higher than 5 weight percent, preferably not higher than 1 weight percent, more preferably not higher than 0.5 weight percent, and most preferably not higher than 0.3 weight percent, considering the uniformity of the true specific gravity of the heat-expandable microspheres A. The existence of aggregated microspheres is identified in the process described above.

[0102] The ratio of microspheres having a true specific gravity not smaller than 0.79 g/cc at 25°C contained in the heat-expandable microspheres A should be not higher than 5 weight percent, preferably not higher than 3 weight percent, more preferably not higher than 2 weight percent, and most preferably not higher than 1 weight percent, considering the uniformity of the true specific gravity of the heat-expandable microspheres A. The ratio of microspheres having a true specific gravity not smaller than 0.79 g/cc is determined by quantitative analysis of the precipitation remained after the separation by specific gravity with isopropyl alcohol (having a specific gravity of 0.79 at 25°C).

[0103] Adhering a particulate filler on the outer surface of the shell of the heat-expandable microspheres A is preferable as explained in “A. Production process for heat-expanded microspheres”. Dispersibility and flowability of the heat-expandable microspheres A are improved with the particulate filler. The same particulate fillers as mentioned above may be applied for the purpose.

An average particle size of the particulate fillers is not particularly limited, but preferably not greater than 10  $\mu\text{m}$ , more preferably not greater than 8  $\mu\text{m}$ , and most preferably not greater than 5  $\mu\text{m}$ .

Keeping the heat-expandable microspheres A in wet state with a liquid organic compound (or water) is preferable, as described above.

[0104] The heat-expandable microspheres A of the present invention contain slight ratios of aggregated microspheres and microspheres having a high true specific gravity. In addition, the heat-expandable microspheres A are durable against collapse by external force owing to their comparatively thick shell of thermoplastic resin. Thus the collapse of heat-expanded microspheres is minimized in mixing with a base component in a process for producing porous material composition containing heat-expanded microspheres. In addition, time-dependent thermal deflation and hardening or shrinking of porous molded products containing heat-expanded microspheres is prevented.

[0105] The heat-expandable microspheres A of the present invention are actually the same as the heat-expanded microspheres, which have a re-expansion initiating temperature and are included in the heat-expanded microspheres mentioned above, and applied to similar field to those for the heat-expanded microspheres.

[0106] D. Porous material composition and porous molded products

The porous material composition of the present invention contains a base component and the heat-expanded microspheres and/or the heat-expandable microspheres A (hereinafter sometimes referred to simply as “microspheres (a)” instead of referring as “heat-expanded microspheres and/or heat-expandable microspheres A”). The microspheres (a) have comparatively thick shell of thermoplastic resin and resistant against collapse from external force in the preparation of porous material composition by blending and kneading several components. In addition, the microspheres (a) have a proper expanding performance to prevent hardening and shrinking of porous material composition in molding, and the resultant porous molded products are free from the troubles of time-dependent thermal deflation.

[0107] The heat-expanded microspheres and/or the heat-expandable microspheres A of the present invention are not particularly limited as long as they are the same as those described above, and preferable heat-expanded microspheres are those having a re-expanding capacity (in other words, having a re-expansion initiating temperature). In addition, microspheres containing lower ratio of aggregated microspheres are preferable. The ratio of aggregated microspheres is preferably not higher than 5 weight percent, more preferably not higher than 3 weight percent, and most preferably not higher than 2 weight percent, considering uniform dispersion of microspheres in a base component, surface finish of resultant porous molded products, and uniformity of their strength. Preferable coefficient of variation, CV, of their particle size distribution is not higher than 30 %, more preferably not higher than 27 %, and most preferably not higher than 25 %.

[0108] The materials applicable as base components of porous material composition are, for example,



organic materials, such as vinyl chloride resin, vinyl acetate resin, acrylic resin, ethylene vinyl acetate resin, epoxy resin, polyurethane, melamine resin, polyester, and silicone resin; and inorganic material, such as ceramic (clay) and cement; though it is not particularly limited. The liquid organic compounds described in the wetting step in the “A. Production process of heat-expanded microspheres” may be blended as the base component. At least one of those base components may be blended.

[0109] The ratio of the microsphere (a) in the whole of the porous material composition should be, but not particularly limited, preferably 0.1 to 30 weight percent, more preferably 0.3 to 25 weight percent, and most preferably 0.5 to 20 weight percent, considering their effect in the composition, lightweight effect, prevention of hardening and shrinking of products in molding, time-dependent thermal deflation of resultant porous molded products, and uniform mixing of porous material composition in production process.

[0110] Fillers conventionally employed for lightweight effect, such as perlite, flyash, sirasu-balloons, glass balloons, phenol balloons, carbon balloons, alumina balloons, and expanded styrene beads; reinforcing agents, such as glass fiber and aramid fiber; fillers, such as silica, talc, and calcium carbonate; and pigments, such as titanium oxide and magnesium oxide may be added to the porous material composition in addition to base components and the microsphere (a). At least one of those additives may be blended.

[0111] Fillers added in porous material composition are apt to cause a trouble of considerable collapse of heat-expanded microspheres or heat-expandable microspheres A due to external force in the production process of porous material composition. The comparatively thick shell of the microspheres contributes to decrease such collapse to great extent.

[0112] The production process of the porous material composition is not particularly limited, as long as the components are mixed. Examples of production devices include static mixers and dispersers.

[0113] The porous material composition may be employed for imparting lightweight effect to putty, paints, sealants, mortars, papier-mâché, and pottery.

[0114] The porous material composition produced in such process attain sufficient lightweight effect, prevents hardening and shrinking of products in molding, eliminating time-dependent thermal deflation of products, and contributes to the production of porous molded products of high dimensional stability. Porous molded products of inorganic materials may be baked to form separated bubbles in the molded inorganic products.

[0115] Examples

The present invention is described specifically with the following examples and comparative examples, though the present invention is not restricted within the scope of those examples.

[0116] Determination procedures and definition

[Determination of average particle size and particle size distribution]

A laser diffraction particle size analyzer (produced by SYMPATEC, HEROS & RODOS) was employed for the determination. Microspheres were analyzed in dry system with a dry dispersion unit, where a dispersion pressure was controlled at 5.0 bar and degree of vacuum was controlled at 5.0 mbar. The D50 value was determined as an average particle size.

5 [0117] [Determination of true specific gravity]

The true specific gravity of microspheres was determined with the liquid substitution method (Archimedean method) with isopropyl alcohol at 25°C.

[0118] [Determination of ratio of aggregated microspheres]

The existence of aggregated microspheres was identified visually with electron microscope.

10 The ratio of aggregated microspheres contained in heat-expanded microspheres (heat-expandable microspheres A) was calculated from the amount of aggregated microspheres remained after screening heat-expanded microspheres (heat-expandable microspheres A) with a sieve of 2.0R sieve opening, where R is the average particle size of screened microspheres, and 2.0R is obtained by multiplying a value “a”, which is greater than or equal to 1.95 and is less than 2.05, with  
15 R. If a sieve of 2.0R sieve opening is not available, the ratio of the residue after screening with a sieve of a sieve opening ranging from 1.8R to 2.0R (except 2.0R) and the ratio of the residue after screening with a sieve of a sieve opening ranging from 2.0R to 2.2R (except 2.0R) are proportionally distributed and calculated to determine an amount equal to the ratio of the residue after screening with a sieve of 2.0R sieve opening. For selecting each of sieves with a sieve opening ranging from 1.8R  
20 to 2.0R (except 2.0R) and from 2.0R to 2.2R (except 2.0R), a sieve having a sieve opening nearest to 2.0R was selected. The amount of a sample screened with a sieve was not smaller than 1 liter.

[0119] [Determination of moisture content in heat-expandable microspheres]

The moisture content was determined with a Karl Fischer moisture meter (MKA-510N, produced by Kyoto Electronics Manufacturing Co., Ltd.).

25 [0120] [Determination of ratio of blowing agent encapsulated in heat-expandable microspheres]

One gram of heat-expandable microspheres was placed in a stainless steel evaporating dish 15 mm deep and 80 mm in diameter, and weighed out ( $W_1$ ). Thirty milliliter of acetone was added to disperse the microspheres uniformly. After being left for 30 minutes at room temperature, the sample was dried at 120°C for 2 hours, and the dry weight ( $W_2$ ) was determined. The ratio of  
30 encapsulated blowing agent was calculated by the following expression.

Ratio of encapsulated blowing agent (%) =  $(W_1 - W_2) \text{ (g)} / 1.0 \text{ (g)} \times 100 - (\text{moisture content})$   
(weight %)

(The moisture content in the expression was calculated as described above.)

[0121] [Determination of retention of encapsulated blowing agent]

35 The retention of an encapsulated blowing agent was the ratio between the ratio of an encapsulated blowing agent after expansion ( $G_2$ ) and the ratio of an encapsulated blowing agent before expansion ( $G_1$ ), and calculated by the following expression.

Retention of encapsulated blowing agent (%) =  $G_2 / G_1 \times 100$

[0122] [Determination of (re-)expansion initiating temperature, maximum (re-)expanding temperature, and expansion coefficient at the temperature ]

Those properties were determined with DMA (DMA Q800, produced by TA Instruments). In an aluminum cup 4.8 mm in depth and 6.0 mm in diameter, 0.5 mg of heat-expandable microspheres (or heat-expanded microspheres) were placed, and an aluminum cover having 0.1 mm thickness and 5.6 mm in diameter was placed on the cup. The sample in the cup was subjected to a pressure of 0.01 N with a weight, and the height of the sample ( $H_1$ ) was measured. The sample was then subjected to elevated temperature rising at a rate of 10°C/min in a range from 20 to 300°C, being subjected to a pressure of 0.01 N with the pressure, and the vertical change of the position of the press was determined. The temperature at which the press started to change its position was determined as a (re-) expansion initiating temperature, and the temperature at which the press indicated a highest position ( $H_2$ ) was determined as the maximum (re-)expanding temperature. A (re-) expansion coefficient, at the maximum (re-) expanding temperature, E, was calculated by the following expression.

$$E (\%) = H_2 / H_1 \times 100$$

[0123] [Volume expansion coefficient]

Volume expansion coefficient (A) was calculated by determining an average particle size ( $R_1$ ) of heat-expandable microspheres before heat-expansion and an average particle size of heat-expandable microspheres ( $R_2$ ), and by calculating the values by the following expression.

$$A = (R_2 / R_1)^3 \text{ (times)}$$

(Where  $R_1$  is an average particle size of heat-expandable microspheres before heat-expansion, and  $R_2$  is an average particle size of heat-expanded microspheres.)

[0124] [Evaluation of running performance of tire filled with microcapsules with normal internal pressure]

Heat-expandable microspheres (or heat-expanded microspheres) were filled in an assembly of a tire (with a size of 175/80R13, and a capacity of 21 liters) and a rim (with a size of 5J-13) to 80 % of the capacity of the assembly, and the internal pressure of the tire was controlled at 200 kPa of gauge pressure with nitrogen. The tire was equipped to an automobile and was run at 60 km/hr for 30 minutes, and the expansion or shrinkage of the heat-expandable microspheres (or heat-expanded microspheres) was checked and evaluated. Expansion of microspheres was identified by measuring their particle size distribution. The difference in the average particle size of microspheres before and after the running was evaluated as ○ for a difference within +3 %, and as × for a difference beyond +3 %. The shrinkage of microspheres was identified and evaluated as ○ in the case that a difference in average particle size before and after the running was within - 3 %, and as × for a difference beyond - 3 %.

[0125] [Evaluation of high-speed running performance of tire filled with microcapsules with normal internal pressure]

The evaluation was performed in the same manner as in the evaluation of running performance of tire filled with microcapsules with normal internal pressure, except that the running speed of an automobile was increased from 60 km/hr to 150 km/hr.

[0126] [Evaluation of running performance of damaged tire filled with microcapsules]

An automobile was driven for 30 minutes in the same manner as in the evaluation of running performance of tire filled with microcapsules with normal internal pressure, except that the running speed of an automobile was increased from 60 km/hr to 100 km/hr. Then the tire was run on a nail having 50 mm length and 3 mm in diameter to make the nail pierce into the tire. After checking that the internal pressure of the tire decreased to the atmospheric pressure, the automobile was run at 90 km/hr. The running performance was evaluated as  $\times$  in the case that the automobile could run in a distance shorter than 80 km, as  $\bigcirc$  in the case that the automobile could run in a distance from 80 to 150 km, and as  $\odot$  in the case that the automobile could run in a distance longer than 150 km.

[0127] [Determination of specific gravity of paint]

The specific gravity of a paint was determined with a specific gravity cup (100 cc, produced by Ohira Rika Kogyo).

[0128] [Determination of specific gravity of coating film]

The specific gravity of a coating film was determined with a liquid substitution method (Archimedean method) with deionized water at 25°C.

[0129] Example A1

Heat-expanded microspheres were produced by heating and expanding MATSUMOTO MICROSPHERE F-50 (produced by Matsumoto Yushi-Seiyaku Co., Ltd., comprising of nitrile copolymer as thermoplastic resin shell, and isobutane as a blowing agent, with the average particle size of 20  $\mu\text{m}$ , and the coefficient of variation of 35 %) with the production machine equipped with the expanding device shown in Figure 1.

The expansion conditions were controlled into 0.1 kg/h for raw material feeding rate, 0.03  $\text{m}^3/\text{min}$  for flow rate of gas containing dispersed raw material, 0.5  $\text{m}^3/\text{min}$  for flow rate of hot gas, and 130°C for hot gas temperature.

The resultant heat-expanded microspheres had an average particle size of 83  $\mu\text{m}$ , a coefficient of variation of 36 %, a true specific gravity of 0.031 g/cc, and the volume expansion coefficient of 71.5. Microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C were not found in the resultant heat-expanded microspheres. No residues remained in each of the screening with the sieves of 150  $\mu\text{m}$  sieve opening and 175  $\mu\text{m}$  sieve opening. The ratio of aggregated microspheres calculated from the result of each screening with proportional distribution was 0 weight percent.

[0130] Comparative Example A1

MATSUMOTO MICROSPHERE F-50, applied in Example A1, was coated on a steel belt approximately in 2 mm thick. The steel belt was driven through a heating zone (at 130°C, 3 m long) and subsequent cooling zone (at 10°C, 2 m long) at a velocity of 1 m/min to produce heat-expanded microspheres.

5 The resultant heat-expanded microspheres had the average particle size of 86  $\mu\text{m}$ , the coefficient of variation of 49 %, the true specific gravity of 0.038 g/cc, and the cubic expansion coefficient of 79.5. In the resultant heat-expanded microspheres, 11 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C was found. The ratio of the residue after screening with the sieve of 150  $\mu\text{m}$  sieve opening was 0.8 weight percent, and the ratio of the  
10 residues after screening with the sieves of 165  $\mu\text{m}$  and 175  $\mu\text{m}$  sieve opening was 0.5 weight percent and 0.4 weight percent, respectively. The ratio of aggregated microspheres calculated from those result with proportional distribution was 0.4 weight percent.

[0131] Example A2

Heat-expanded microspheres were produced in the same manner as in Example A1, except that  
15 the heat-expandable microspheres, MATSUMOTO MICROSPHERE F-50, were replaced with MATSUMOTO MICROSPHERE F-100 (produced by Matsumoto Yushi-Seiyaku Co., Ltd., comprising of nitrile copolymer as thermoplastic resin shell, and isopentane as a blowing agent, with the average particle size of 25  $\mu\text{m}$  and the coefficient of variation of 37 %), and that the hot gas temperature was controlled at 180°C.

20 The resultant heat-expanded microspheres had the average particle size of 97  $\mu\text{m}$ , the coefficient of variation of 36 %, the true specific gravity of 0.028 g/cc, and the cubic expansion coefficient of 58.4. Microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C were not found in the resultant heat-expanded microspheres. No residue was remained in the screening with the sieve of 200  $\mu\text{m}$  sieve opening. No residue was remained in each of the screening  
25 with the sieve of 175  $\mu\text{m}$  sieve opening and with the sieve of 210  $\mu\text{m}$  sieve opening. The ratio of aggregated microspheres calculated from those results with proportional distribution was 0 weight percent.

[0132] Comparative Example A2

Heat-expanded microspheres were produced in the same manner as in Comparative Example  
30 A1, except that MATSUMOTO MICROSPHERE F-50 was replaced with MATSUMOTO MICROSPHERE F-100 and that the heating zone temperature was controlled at 180°C.

The resultant heat-expanded microspheres had the average particle size of 100  $\mu\text{m}$ , the coefficient of variation of 45 %, the true specific gravity of 0.030 g/cc, and the cubic expansion coefficient of 64.0. In the resultant heat-expanded microspheres, 0.3 weight percent of aggregated  
35 microspheres and 15 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C were found. The amount of aggregated microspheres was determined with the sieve of 200  $\mu\text{m}$  sieve opening.

## [0133] Example A3

Heat-expanded microspheres were produced in the same manner as in Example A1, except that the heat-expandable microspheres, MATSUMOTO MICROSPHERE F-50, were replaced with a trial product 1 of heat-expandable microspheres (comprising of nitrile copolymer as thermoplastic resin shell, and isohexane as a blowing agent, with the average particle size of 35  $\mu\text{m}$  and the coefficient of variation of 20 %), and the hot gas temperature was controlled at 240°C.

The resultant heat-expanded microspheres had the average particle size of 130  $\mu\text{m}$ , the coefficient of variation of 20 %, the true specific gravity of 0.021 g/cc, and the cubic expansion coefficient of 51.1. Microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C were not found in the resultant heat-expanded microspheres. No residue was remained in the screening with the sieve of 200  $\mu\text{m}$  sieve opening. No residue was remained in each of the screening with the sieves of 235  $\mu\text{m}$  sieve opening and 275  $\mu\text{m}$  sieve opening. The ratio of aggregated microspheres calculated from those results with proportional distribution was 0 weight percent.

## [0134] Comparative Example A3

Heat-expanded microspheres were produced in the same manner as in Comparative Example A1, except that MATSUMOTO MICROSPHERE F-50 was replaced with the trial product 1 of heat-expandable microspheres described in Example A3 and that the heating zone temperature was controlled at 240°C.

The resultant heat-expanded microspheres had the average particle size of 100  $\mu\text{m}$ , the coefficient of variation of 31 %, the true specific gravity of 0.030 g/cc, and the cubic expansion coefficient of 66.6. The resultant heat-expanded microspheres contained 5.6 weight percent of aggregated microspheres and 12 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C. The amount of aggregated microspheres was determined with the sieve of 200  $\mu\text{m}$  sieve opening.

## [0135] Example A4

The trial product 1 of heat-expandable microspheres described in Example A3 and ultrafine powder talc (produced by Nihon Talc Co., Ltd, with a trade name, SG-1000, with the average particle size of 2.0  $\mu\text{m}$ ) was mixed in 6:4 weight ratio uniformly with a Super Mixer (manufactured by Kawata MFG Co., Ltd.) to produced heat-expandable microspheres with outer surface on which the ultrafine powder talc was adhered.

Heat-expanded microspheres were produced in the same manner as in Example A1, except that the heat-expandable microspheres, MATSUMOTO MICROSPHERE F-50, were replaced with the heat-expandable microspheres with outer surface on which ultrafine powder talc was adhered and the hot gas temperature was controlled at 240°C.

The resultant heat-expanded microspheres had the average particle size of 124  $\mu\text{m}$ , the coefficient of variation of 21 %, the true specific gravity of 0.026 g/cc, and the cubic expansion coefficient of 44.4. Microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C

were not found in the resultant heat-expanded microspheres. No residue was remained in the screening with the sieve of 200  $\mu\text{m}$  sieve opening. No residue was remained in each of the screening with the sieves of 225  $\mu\text{m}$  sieve opening and 250  $\mu\text{m}$  sieve opening. The ratio of aggregated microspheres calculated from those results with proportional distribution was 0 weight percent.

5 [0136] Example B1

Heat-expanded microspheres were produced by thermally expanding MATSUMOTO MICROSPHERE F-50 (produced by Matsumoto Yushi-Seiyaku Co., Ltd., comprising of nitrile copolymer as thermoplastic resin shell, and isobutane as a blowing agent, with the average particle size of 20  $\mu\text{m}$  and the coefficient of variation of 35 %) with the production machine equipped with the expanding device shown in Figure 2.

The expanding parameters were controlled into 0.1 kg/h for raw material feeding rate, 0.05  $\text{m}^3/\text{min}$  for flow rate of gas containing dispersed raw material, 1.0  $\text{m}^3/\text{min}$  for flow rate of hot gas, and 140°C for hot gas temperature.

The resultant heat-expanded microspheres had the average particle size of 98  $\mu\text{m}$ , the coefficient of variation of 36 %, the true specific gravity of 0.022 g/cc, and the cubic expansion coefficient of 117.6. Microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C were not found in the resultant heat-expanded microspheres. No residue was remained in the screening with the sieve of 150  $\mu\text{m}$  sieve opening. No residue was remained in each of the screening with the sieves of 180  $\mu\text{m}$  sieve opening and 200  $\mu\text{m}$  sieve opening. The ratio of aggregated microspheres calculated from the result of each screening with proportional distribution was 0 weight percent.

[0137] Comparative Example B1

MATSUMOTO MICROSPHERE F-50, applied in Example B1, was coated on a steel belt approximately in 2 mm thick. The steel belt was driven through a heating zone (at 130°C, 3 m long) and subsequent cooling zone (at 10°C, 2 m long) at a velocity of 1 m/min to produce heat-expanded microspheres.

The resultant heat-expanded microspheres had the average particle size of 102  $\mu\text{m}$ , the coefficient of variation of 48 %, the true specific gravity of 0.020 g/cc, and the cubic expansion coefficient of 132.7. In the resultant heat-expanded microspheres, 12 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C was found. The ratio of the residue after screening with the sieve of 150  $\mu\text{m}$  sieve opening was 1.8 weight percent, and the ratio of the residue after each of the screening with the sieves of 165  $\mu\text{m}$  sieve opening and 175  $\mu\text{m}$  sieve opening was 0.8 weight percent and 0.5 weight percent, respectively. The ratio of aggregated microspheres calculated from those result with proportional distribution was 0.7 weight percent.

35 [0138] Example B2

Heat-expanded microspheres were produced in the same manner as in Example B1, except that the heat-expandable microspheres, MATSUMOTO MICROSPHERE F-50, were replaced with

MATSUMOTO MICROSPHERE F-100 (produced by Matsumoto Yushi-Seiyaku Co., Ltd., comprising of nitrile copolymer as thermoplastic resin shell, and isopentane as a blowing agent, with the average particle size of 25  $\mu\text{m}$  and the coefficient of variation of 37 %), and that the hot gas temperature was controlled at 170°C.

5        The resultant heat-expanded microspheres had the average particle size of 93  $\mu\text{m}$ , the coefficient of variation of 38 %, the true specific gravity of 0.033 g/cc, and the cubic expansion coefficient of 51.5. Microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C were not found in the resultant heat-expanded microspheres. No residue was remained in each of the screening with the sieves of 175  $\mu\text{m}$  sieve opening and 200  $\mu\text{m}$  sieve opening. The ratio of  
10 aggregated microspheres calculated from those results with proportional distribution was 0 weight percent.

[0139] Comparative Example B2

Heat-expanded microspheres were produced in the same manner as in Comparative Example B1, except that MATSUMOTO MICROSPHERE F-50 was replaced with MATSUMOTO  
15 MICROSPHERE F-100 and that the heating zone temperature was controlled at 170°C.

The resultant heat-expanded microspheres had the average particle size of 85  $\mu\text{m}$ , the coefficient of variation of 48 %, the true specific gravity of 0.040 g/cc, and the cubic expansion coefficient of 39.3. The resultant heat-expanded microspheres contained 14 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C. The ratio of the  
20 residue after screening with the sieve of 200  $\mu\text{m}$  sieve opening was 0.8 weight percent, and the ratio of the residue after each of the screening with the sieves of 165  $\mu\text{m}$  sieve opening and 175  $\mu\text{m}$  sieve opening was 2.5 weight percent and 1.8 weight percent, respectively. The ratio of aggregated microspheres calculated from those results with proportional distribution was 2.2 weight percent.

[0140] Example B3

25        Heat-expanded microspheres were produced in the same manner as in Example B1, except that the heat-expandable microspheres, MATSUMOTO MICROSPHERE F-50, were replaced with the trial product 1 of heat-expandable microspheres (comprising of nitrile copolymer as thermoplastic resin shell, and isohexane as a blowing agent, having the average particle size of 35  $\mu\text{m}$  and the coefficient of variation of 20 %), and the hot gas temperature was controlled at 230°C.

30        The resultant heat-expanded microspheres had the average particle size of 120  $\mu\text{m}$ , the coefficient of variation of 21 %, the true specific gravity of 0.027 g/cc, and the cubic expansion coefficient of 40.3. Microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C were not found in the resultant heat-expanded microspheres. No residue was remained in the screening with the sieve of 200  $\mu\text{m}$  sieve opening. No residue was remained in each of the screening  
35 with the sieves of 225  $\mu\text{m}$  sieve opening and 250  $\mu\text{m}$  sieve opening. The ratio of aggregated microspheres calculated from those results with proportional distribution was 0 weight percent.

[0141] Comparative Example B3



Heat-expanded microspheres were produced in the same manner as in Comparative Example B1, except that MATSUMOTO MICROSPHERE F-50 was replaced with the trial product 1 of heat-expandable microspheres described in Example B3 and that the heating zone temperature was controlled at 230°C.

5 The resultant heat-expanded microspheres had the average particle size of 117  $\mu\text{m}$ , the coefficient of variation of 31 %, the true specific gravity of 0.031 g/cc, and the cubic expansion coefficient of 37.3. The resultant heat-expanded microspheres contained 15 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C. The ratio of the residue after screening with the sieve of 200  $\mu\text{m}$  sieve opening was 6.6 weight percent, and the ratio  
10 of the residue after each of the screening with the sieves of 215  $\mu\text{m}$  sieve opening and 250  $\mu\text{m}$  sieve opening was 5.6 weight percent and 3.2 weight percent, respectively. The ratio of aggregated microspheres calculated from those results with proportional distribution was 4.3 weight percent.

[0142] Example B4

Heat-expandable microspheres were produced by uniformly blending the trial product 1 of  
15 heat-expandable microspheres described in Example B3 and ultrafine powder talc (produced by Nihon Talc Co., Ltd., with a trade name, SG-1000, having an average particle size of 2.0  $\mu\text{m}$ ) in a 6:4 weight ratio with a Super Mixer (manufactured by Kawata MFG Co., Ltd.) to adsorb ultrafine powder talc on the outer surface of the heat-expandable microspheres.

Heat-expanded microspheres were produced in the same manner as in Example B1, except that  
20 MATSUMOTO MICROSPHERE F-50 were replaced with the heat-expandable microspheres with outer surface on which ultrafine powder talc was adhered, and the hot gas temperature was controlled at 230°C.

The resultant heat-expanded microspheres had the average particle size of 119  $\mu\text{m}$ , the coefficient of variation of 21 %, the true specific gravity of 0.029 g/cc, and the cubic expansion  
25 coefficient of 39.3. Microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C were not found in the resultant heat-expanded microspheres. No residue was remained in the screening with the sieve of 200  $\mu\text{m}$  sieve opening. No residue was remained in each of the screening with the sieves of 225  $\mu\text{m}$  sieve opening and 250  $\mu\text{m}$  sieve opening. The ratio of aggregated microspheres calculated from those results with proportional distribution was 0 weight percent.

30 [0143] Example C1

An aqueous phase was prepared by adding 150 g of sodium chloride, 3.0 g of an adipic acid-diethanolamine condensate, 20 g of colloidal silica (20 % concentration), and 0.15 g of sodium nitrite to 500 g of deionized water, and by homogenizing the mixture with agitation.

An oily phase was prepared by mixing 180 g of acrylonitrile, 45 g of methacrylonitrile, 75 g of  
35 methacrylic acid, 1.2 g of trimethylolpropane trimethacrylate, 2.0 g of azobisisobutyronitrile, and 150 g of  $\text{C}_3\text{F}_7\text{OCH}_3$ , and agitating to dissolve the ingredients.

[0144] Then the aqueous phase and the oily phase were mixed preliminarily with a homogenizer at

3,000 rpm for 2 minutes, and then agitated at 10,000 rpm for 2 minutes to prepare a suspension. Then, the suspension was transferred into a reactor, purged with nitrogen, and polymerized at 61°C for 20 hours with agitation. The polymerization product was filtered and dried. The resultant microspheres had an average particle size of 25  $\mu\text{m}$ , a CV or coefficient of variation of 24 %, an expansion initiating temperature of 143°C, and the maximum expanding temperature of 205°C.

The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 31.8 weight percent.

The microspheres did not burn when a source of ignition was brought close to them.

[0145] The resultant heat-expandable microspheres were processed into heat-expanded microspheres by heating and expanding with the production machine equipped with the expanding device shown in Figure 1.

Some of the expanding parameters were controlled constant, 1.0 kg/h for the raw material feeding rate, 0.05  $\text{m}^3/\text{min}$  for the flow rate of gas containing dispersed raw material, and 0.5  $\text{m}^3/\text{min}$  for the flow rate of hot gas, while the hot gas temperature was controlled into varied levels, 300°C, 350°C, 400°C, 450°C, and 500°C, as shown in Table 1.

The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and the results were described in Table 1.

[0146] Table 1

	Hot gas temperature				
	300°C	350°C	400°C	450°C	500°C
Sample number	No. 1	No. 2	No. 3	No. 4	No. 5
Average particle size ( $\mu\text{m}$ )	74.8	89.5	111	124	136
Coefficient of variation, CV (%)	24	24	25	24	25
Ratio of encapsulated blowing agent (%)	31.5	31.5	31.2	30.9	31.0
Retention of encapsulated blowing agent (%)	99.0	98.4	98.1	97.3	97.5
True specific gravity (g/cc)	0.046	0.028	0.014	0.010	0.008
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	1.1	0.8	0.4	0.4	0.4
Opening of Sieve 1 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	150/0	175/0	200/0	250/0	270/0
Opening of Sieve 2 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	---	185/0	225/0	---	280/0
Ratio of aggregated microspheres (weight percent)	0	0	0	0	0
(Re-) Expansion initiating temperature (°C)	131	132	131	132	133
Maximum (re-) expanding temperature (°C)	203	202	202	202	202
(Re-) Expansion coefficient (%)	240	211	160	120	101
Running performance of microsphere-filled tire with normal internal pressure at driving	○	○	○	○	○
Running performance of microsphere-filled tire with normal internal pressure at high speed driving	○	○	○	○	○
Running performance of damaged microsphere-filled tire	◎	◎	○	○	○

As clearly shown in the result in Table 1, the heat-expandable microspheres produced in this Example exhibited superior performance in the evaluation of the running performance with normal internal pressure, the running performance with normal internal pressure at high speed, and the running performance of damaged tire, when they were filled in a tire-and-rim assembly.

5 [0147] Comparative Example C1

The heat-expandable microspheres produced in Example C1 was processed into heat-expanded microspheres with heating for 1 minute in an oven (produced by Sanyo Electric Co.), with hot gas temperature being controlled at different levels, 140°C, 160°C, 180°C, 200°C, and 220°C, as described in Table 2.

10 The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 2.

[0148] Table 2

	Hot gas temperature				
	140°C	160°C	180°C	200°C	220°C
Sample number	No. 6	No. 7	No. 8	No. 9	No. 10
Average particle size (μm)	89.6	104	126	148	169
Coefficient of variation, CV (%)	27	25	24	24	25
Ratio of encapsulated blowing agent (%)	31.5	31.2	31.1	30.3	29.9
Retention of encapsulated blowing agent (%)	99.2	98.2	97.8	95.3	94.1
True specific gravity (g/cc)	0.083	0.038	0.029	0.015	0.011
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	23.1	18.7	8.9	7.5	6.9
Opening of Sieve 1 (μm)/ratio of aggregated microspheres in the screening (weight percent)	175/1.0	200/2.7	250/3.2	300/6.9	330/11.3
Opening of Sieve 2 (μm)/ratio of aggregated microspheres in the screening (weight percent)	185/0.7	215/1.2	---	---	350/2.5
Ratio of aggregated microspheres (weight percent)	0.9	2.3	3.2	6.9	7.8
(Re-) Expansion initiating temperature (°C)	178	179	178	179	178
Maximum (re-) expanding temperature (°C)	223	223	222	223	223
(Re-) Expansion coefficient (%)	209	167	142	134	120
Running performance of microsphere-filled tire with normal internal pressure at driving	○	○	○	○	○
Running performance of microsphere-filled tire with normal internal pressure at high speed driving	×	×	×	×	×
Running performance of damaged microsphere-filled tire	○	○	○	×	×

15 As clearly shown in the result in Table 2, the heat-expandable microspheres, which were produced in this Comparative Example, exhibited superior performance in the evaluation of the running performance with normal internal pressure but exhibited poor performance in the evaluation of the running performance with normal internal pressure at high speed, when they were filled in a tire-and-rim assembly. The cause of the poor performance is estimated to be the high ratio of microspheres having a true specific gravity not lower than 0.79 g/cc.

As clearly shown in the comparison of the ratio of aggregated microspheres in the microspheres of Example C1 and Comparative Example C1, conventional expanding processes, such as heating in an oven, cannot process heat-expandable microspheres with uniform particle size distribution, which are employed as raw material microspheres, into heat-expanded microspheres with uniform particle size distribution containing no aggregated microspheres.

[0149] Example C2

The polymerization was performed in the same manner as in Example C1 except that 150 g of  $C_3F_7OCH_3$  (with the specific gravity of 1.41) was replaced with 65 g of normal pentane (with the specific gravity of 0.63).

The resultant heat-expandable microspheres had the average particle size of 30  $\mu m$ , the CV or coefficient of variation of 33 %, the expansion initiating temperature of 155°C, and the maximum expanding temperature of 189°C. The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 16.6 weight percent.

The microspheres burnt when a source of ignition was brought close to them, and thus the evaluation of the microspheres being filled in a tire-and-rim assembly was abandoned.

[0150] The resultant heat-expandable microspheres were processed into heat-expanded microspheres by heating and expanding with the production machine equipped with the expanding device shown in Figure 1. Some of the expanding parameters were controlled constant, 1.0 kg/h for the raw material feeding rate, 0.05  $m^3/min$  for the flow rate of gas containing dispersed raw material, and 0.5  $m^3/min$  for the flow rate of hot gas, while the hot gas temperature was controlled into varied levels, 300°C, 350°C, 400°C, 450°C, and 500°C. The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 3.

[0151] Table 3

	Hot gas temperature				
	300°C	350°C	400°C	450°C	500°C
Sample number	No. 11	No. 12	No. 13	No. 14	No. 15
Average particle size ( $\mu m$ )	75.4	84.1	107	137	122
Coefficient of variation, CV (%)	34	33	33	34	36
Ratio of encapsulated blowing agent (%)	14.7	13.3	12.9	11.2	8.9
Retention of encapsulated blowing agent (%)	88.3	80.1	77.8	67.4	53.6
True specific gravity (g/cc)	0.066	0.045	0.022	0.010	0.015
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	4.2	3.5	3.4	3.1	2.5
Opening of Sieve 1 ( $\mu m$ )/ratio of aggregated microspheres in the screening (weight percent)	150/0	150/0.5	215/0.1	275/0.3	225/3.3
Opening of Sieve 2 ( $\mu m$ )/ratio of aggregated microspheres in the screening (weight percent)	---	175/0.1	---	---	250/1.0
Ratio of aggregated microspheres (weight percent)	0	0.2	0.1	0.3	1.4
(Re-) Expansion initiating temperature (°C)	133	132	132	133	none
Maximum (re-) expanding temperature (°C)	188	187	188	186	none
(Re-) Expansion coefficient (%)	180	148	121	101	none

## [0152] Comparative Example C2

The polymerization was performed in the same manner as in Example C1 except that 75 g of methacrylic acid was replaced with 75 g of vinyl acetate.

5 The resultant heat-expandable microspheres had the average particle size of 27  $\mu\text{m}$ , the CV or coefficient of variation of 25 %, the expansion initiating temperature of 95°C, and the maximum expanding temperature of 157°C. The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 30.9 weight percent. The microspheres did not burn when a source of ignition was brought close to them.

10 [0153] The heat-expandable microspheres produced above was processed into heat-expanded microspheres with heating for 1 minute with an oven (produced by Sanyo Electric Co.), with hot gas temperature being controlled at different levels, 110°C, 130°C, 150°C, 170°C, and 190°C as described in Table 4. The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 4.

15 [0154] Table 4

	Hot gas temperature				
	110°C	130°C	150°C	170°C	190°C
Sample number	No. 16	No. 17	No. 18	No. 19	No. 20
Average particle size ( $\mu\text{m}$ )	80.1	93.2	119	133	154
Coefficient of variation, CV (%)	25	24	25	26	25
Ratio of encapsulated blowing agent (%)	29.5	29.3	28.8	28.8	28.6
Retention of encapsulated blowing agent (%)	95.4	94.7	93.3	93.1	92.6
True specific gravity (g/cc)	0.048	0.032	0.016	0.011	0.017
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	13.4	9.9	8.3	7.9	6.1
Opening of Sieve 1 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	150/6.3	185/5.9	225/7.5	265/6.8	300/8.9
Opening of Sieve 2 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	175/3.8	---	250/4.8	---	350/5.9
Ratio of aggregated microspheres (weight percent)	5.3	5.9	6.1	6.8	8.1
(Re-) Expansion initiating temperature (°C)	83	83	82	none	none
Maximum (re-) expanding temperature (°C)	145	146	146	none	none
(Re-) Expansion coefficient (%)	197	138	106	none	none
Running performance of microsphere-filled tire with normal internal pressure	×	×	×	×	×
Running performance of microsphere-filled tire with normal internal pressure at high speed	×	×	×	×	×
Running performance of damaged microsphere-filled tire	○	×	×	×	×

As clearly shown in the result in Table 4, the heat-expandable microspheres produced in this Comparative Example exhibited poor performance in the evaluation of the running performance with normal internal pressure and the running performance with normal internal pressure at high speed,

though they exhibited proper performance in the evaluation of the running performance of damaged tire in some cases, when they were filled in a tire-and-rim assembly. The cause of the poor performance is estimated as that the temperature of the heat-expandable microspheres in a tire may have reached to their (re-) expansion initiating temperature during the tire was running.

5 [0155] Example C3

The polymerization was performed in the same manner as in Example C1 except that the oily medium was prepared by mixing 235 g of acrylonitrile, 60 g of methacrylonitrile, 5.0 g of methyl methacrylate, 1.2 g of ethyleneglycol dimethacrylate, 2.0 g of azobisisobutyronitrile, and 150 g of  $C_3HF_6OCH_3$ .

10 The resultant microspheres had the average particle size of 42  $\mu m$ , the CV or coefficient of variation of 26 %, the expansion initiating temperature of 140°C, and the maximum expanding temperature of 198°C.

The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 32.9 weight percent. The microspheres did not burn when a source of ignition was brought close to them.

[0156] The resultant heat-expandable microspheres were processed into heat-expanded microspheres by heating and expanding with the production machine equipped with the expanding device shown in Figure 1. Some of the expanding parameters were controlled constant, 1.0 kg/h for the raw material feeding rate, 0.05  $m^3/min$  for the flow rate of gas containing dispersed raw material, and 0.5  $m^3/min$  for the flow rate of hot gas, while the hot gas temperature was controlled into varied levels, 250°C, 300°C, 350°C, 400°C, and 450°C as shown in Table 5. The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 5.

[0157] Table 5

	Hot gas temperature				
	250°C	300°C	350°C	400°C	450°C
Sample number	No.	No.	No.	No.	No.
Average particle size ( $\mu m$ )	108	122	139	166	183
Coefficient of variation, CV (%)	25	26	25	25	27
Ratio of encapsulated blowing agent (%)	32.0	31.5	31.7	31.3	31.1
Retention of encapsulated blowing agent (%)	97.2	95.8	96.3	95.3	94.4
True specific gravity (g/cc)	0.072	0.051	0.034	0.020	0.014
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	1.2	0.8	0.6	0.4	0.2
Opening of Sieve 1 ( $\mu m$ )/ratio of aggregated microspheres in the screening (weight percent)	215/0	225/0	270/0	330/0	350/0
Opening of Sieve 2 ( $\mu m$ )/ratio of aggregated microspheres in the screening (weight percent)	---	250/0	280/0	---	370/0
Ratio of aggregated microspheres (weight percent)	0	0	0	0	0
(Re-) Expansion initiating temperature (°C)	96	96	95	95	96
Maximum (re-) expanding temperature (°C)	197	197	198	197	196
(Re-) Expansion coefficient (%)	240	218	202	147	113

Running performance of microsphere-filled tire with normal internal pressure	○	○	○	○	○
Running performance of microsphere-filled tire with normal internal pressure at high speed driving	×	×	×	×	×
Running performance of damaged microsphere-filled tire	◎	◎	○	○	○

As clearly shown in the result in Table 5, the heat-expandable microspheres produced in this Example exhibited superior performance in the evaluations of the running performance with normal internal pressure and the running performance of damaged tire, when they were filled in a tire-and-rim assembly.

#### Comparative Example C3

The polymerization was performed in the same manner as in Example C3 except that 5.0 g of methyl methacrylate was replaced with 5.0 g of methacrylic acid

The resultant heat-expandable microspheres had the average particle size of 40  $\mu\text{m}$ , the CV or coefficient of variation of 26 %, the expansion initiating temperature of 143°C, and the maximum expanding temperature of 199°C. The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 31.8 weight percent. The microspheres did not burn when a source of ignition was brought close to them.

[0158] The heat-expandable microspheres produced in the above was processed into heat-expanded microspheres with heating for 1 minutes with an oven (produced by Sanyo Electric Co.), with hot gas temperature being controlled at different levels, 120°C, 140°C, 160°C, 180°C, and 200°C as described in Table 6. The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 6.

[0159] Table 6

	Hot gas temperature				
	120°C	140°C	160°C	180°C	200°C
Sample number	No. 26	No. 27	No. 28	No. 29	No. 30
Average particle size ( $\mu\text{m}$ )	98.9	124	144	167	189
Coefficient of variation, CV (%)	26	26	27	27	26
Ratio of encapsulated blowing agent (%)	29.6	29.5	29.3	28.7	28.7
Retention of encapsulated blowing agent (%)	93.1	92.9	92.1	90.4	90.2
True specific gravity (g/cc)	0.086	0.044	0.028	0.018	0.013
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	8.9	7.3	6.3	5.9	5.1
Opening of Sieve 1 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	200/0	250/0.3	280/3.3	330/3.8	385/5.1
Opening of Sieve 2 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	---	---	300/0.9	350/0.4	---
Ratio of aggregated microspheres (weight percent)	0	0.3	2.3	3.1	5.1
(Re-) Expansion initiating temperature (°C)	98	98	99	98	97
Maximum (re-) expanding temperature (°C)	199	199	201	199	197

(Re-) Expansion coefficient (%)	232	206	198	138	107
Running performance of microsphere-filled tire with normal internal pressure	○	○	○	○	○
Running performance of microsphere-filled tire with normal internal pressure at high speed driving	×	×	×	×	×
Running performance of damaged microsphere-filled tire	◎	◎	○	○	○

As clearly shown in the result in Table 6, the heat-expandable microspheres produced in this Comparative Example exhibited poor performance in the evaluation of the running performance with normal internal pressure at high speed, though they exhibited superior performance in the evaluation of the running performance with normal internal pressure, and the running performance of damaged tire, when they were filled in a tire-and-rim assembly.

[0160] Example C4

Heat-expandable microspheres with outer surface on which magnesium stearate was adhered were produced by blending 500 g of the heat-expandable microspheres produced in Example C1 and 100 g of magnesium stearate (having an average particle size of 2.0  $\mu\text{m}$  and a melting point of 132°C) with a Super Mixer (manufactured by Kawata MFG Co., Ltd.) for 30 minutes.

The resultant heat-expandable microspheres had the average particle size of 24.9  $\mu\text{m}$  and the CV or coefficient of variation of 25 %. The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 30.4 weight percent.

[0161] The resultant heat-expandable microspheres were processed into heat-expanded microspheres by heating and expanding with the production machine equipped with the expanding device shown in Figure 1. Some of the expanding parameters were controlled constant, 1.0 kg/h for the raw material feeding rate, 0.05  $\text{m}^3/\text{min}$  for the flow rate of gas containing dispersed raw material, and 0.5  $\text{m}^3/\text{min}$  for the flow rate of hot gas, while the hot gas temperature was controlled into varied levels, 300°C, 350°C, 400°C, 450°C, and 500°C as shown in Table 7. The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 7.

[0162] Table 7

	Hot gas temperature				
	300°C	350°C	400°C	450°C	500°C
Sample number	No. 31	No. 32	No. 33	No. 34	No. 35
Average particle size ( $\mu\text{m}$ )	72.1	87.4	107	118	131
Coefficient of variation, CV (%)	24	24	25	24	25
Ratio of encapsulated blowing agent (%)	29.7	29.4	29.4	29.0	29.1
Retention of encapsulated blowing agent (%)	97.8	96.6	96.6	95.4	95.7
True specific gravity (g/cc)	0.047	0.029	0.016	0.011	0.009
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	1.2	1.1	0.8	0.6	0.5
Opening of Sieve 1 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	140/0	175/0	215/0	215/0	250/0



Opening of Sieve 2 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	150/0	---	---	250/0	270/0
Ratio of aggregated microspheres (weight percent)	0	0	0	0	0
(Re-) Expansion initiating temperature ( $^{\circ}\text{C}$ )	130	133	132	131	133
Maximum (re-) expanding temperature ( $^{\circ}\text{C}$ )	202	203	202	201	202
(Re-) Expansion coefficient (%)	238	222	156	116	103
Running performance of microsphere-filled tire with normal internal pressure	○	○	○	○	○
Running performance of microsphere-filled tire with normal internal pressure at high speed driving	○	○	○	○	○
Running performance of damaged microsphere-filled tire	◎	◎	◎	◎	○

As clearly shown in the result in Table 7, the heat-expandable microspheres produced in this Example exhibited superior performance in the evaluation of the running performance with normal internal pressure, the running performance with normal internal pressure at high speed, and the running performance of damaged tire, when they were filled in a tire-and-rim assembly. The running performance of damaged tire was especially better than the running performance of damaged tire in Example C1 owing to the effect of the anti-blocking agent.

#### [0163] Example C5

Heat-expandable microspheres with outer surface on which carbon black was adhered were produced by blending 500 g of the heat-expandable microspheres produced in Example C1 and 100 g of carbon black (acetylene black having the average particle size of 42 nm) with a Super Mixer (manufactured by Kawata MFG Co., Ltd.) for 30 minutes.

The resultant heat-expandable microspheres had the average particle size of 24.7  $\mu\text{m}$  and the CV or coefficient of variation of 26 %. The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 30.8 weight percent.

[0164] The resultant heat-expandable microspheres were processed into heat-expanded microspheres by heating and expanding with the production machine equipped with the expanding device shown in Figure 1. Some of the expanding parameters were controlled constant, 1.0 kg/h for the raw material feeding rate, 0.05  $\text{m}^3/\text{min}$  for the flow rate of gas containing dispersed raw material, and 0.5  $\text{m}^3/\text{min}$  for the flow rate of hot gas, while the hot gas temperature was controlled into varied levels, 300 $^{\circ}\text{C}$ , 350 $^{\circ}\text{C}$ , 400 $^{\circ}\text{C}$ , 450 $^{\circ}\text{C}$ , and 500 $^{\circ}\text{C}$  as shown in Table 8. The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 8.

#### [0165] Table 8

	Hot gas temperature				
	300 $^{\circ}\text{C}$	350 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$	450 $^{\circ}\text{C}$	500 $^{\circ}\text{C}$
Sample number	No. 36	No. 37	No. 38	No. 39	No. 40
Average particle size ( $\mu\text{m}$ )	73.1	88.6	109	121	134
Coefficient of variation, CV (%)	25	25	26	26	25
Ratio of encapsulated blowing agent (%)	30.1	30.0	29.5	29.6	29.2

Retention of encapsulated blowing agent (%)	97.8	97.4	95.9	96.2	94.7
True specific gravity (g/cc)	0.048	0.032	0.015	0.012	0.007
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	1.3	1.0	0.9	0.5	0.6
Opening of Sieve 1 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	140/0	175/0	215/0	215/0	250/0
Opening of Sieve 2 ( $\mu\text{m}$ )/ratio of aggregated microspheres in the screening (weight percent)	150/0	---	---	250/0	270/0
Ratio of aggregated microspheres (weight percent)	0	0	0	0	0
(Re-) Expansion initiating temperature ( $^{\circ}\text{C}$ )	130	133	132	131	133
Maximum (re-) expanding temperature ( $^{\circ}\text{C}$ )	202	203	202	201	202
(Re-) Expansion coefficient (%)	239	225	163	118	101
Running performance of microsphere-filled tire with normal internal pressure	○	○	○	○	○
Running performance of microsphere-filled tire with normal internal pressure at high speed driving	○	○	○	○	○
Running performance of damaged microsphere-filled tire	⊙	⊙	⊙	⊙	○

As clearly shown in the result in Table 8, the heat-expandable microspheres produced in this Example exhibited superior performance in the evaluation of the running performance with normal internal pressure, the running performance with normal internal pressure at high speed, and the running performance of damaged tire, when they were filled in a tire-and-rim assembly. The running performance of damaged tire was especially better than the running performance of damaged tire of the Example C1 owing to the effect of the anti-blocking agent.

#### [0166] Example C6

The polymerization was performed in the same manner as in Example C1 except that the oily medium was prepared by mixing 120 g of acrylonitrile, 30 g of methacrylonitrile, 150 g of methacrylic acid, 1.2 g of trimethylolpropane trimethacrylate, 2.0 g of azobisisobutyronitrile, and 150 g of  $\text{C}_2\text{HF}_4\text{OC}_2\text{H}_2\text{F}_3$ .

The resultant microspheres had the average particle size of 29  $\mu\text{m}$ , the CV or coefficient of variation of 23 %, the expansion initiating temperature of 183 $^{\circ}\text{C}$ , and the maximum expanding temperature of 230 $^{\circ}\text{C}$ . The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 32.5 weight percent. The microspheres did not burn when a source of ignition was brought close to them.

[0167] The resultant heat-expandable microspheres were processed into heat-expanded microspheres by heating and expanding with the production machine equipped with the expanding device shown in Figure 2, which is described in "Production process of heat-expanded microspheres". Some of the expanding parameters were controlled constant, 1.0 kg/h for the raw material feeding rate, 0.05  $\text{m}^3/\text{min}$  for the flow rate of gas containing dispersed raw material, and 0.5  $\text{m}^3/\text{min}$  for the flow rate of hot gas, while the hot gas temperature was controlled into varied levels, 400 $^{\circ}\text{C}$ , 450 $^{\circ}\text{C}$ , 500 $^{\circ}\text{C}$ , 550 $^{\circ}\text{C}$ ,

and 600°C as shown in Table 9. The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 9.

[0168] Table 9

	Hot gas temperature				
	400°C	450°C	500°C	550°C	600°C
Sample number	No. 41	No. 42	No. 43	No. 44	No. 45
Average particle size (μm)	78.9	95.1	107	120	137
Coefficient of variation, CV (%)	24	23	23	24	23
Ratio of encapsulated blowing agent (%)	32.1	32.0	32.0	32.0	31.9
Retention of encapsulated blowing agent (%)	98.9	98.5	98.5	98.5	98.2
True specific gravity (g/cc)	0.063	0.036	0.025	0.018	0.012
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	1.9	1.3	0.9	0.6	0.3
Opening of Sieve 1 (μm)/ratio of aggregated microspheres in the screening (weight percent)	150/0	185/0	215/0	225/0	270/0
Opening of Sieve 2 (μm)/ratio of aggregated microspheres in the screening (weight percent)	175/0	200/0	---	250/0	---
Ratio of aggregated microspheres (weight percent)	0	0	0	0	0
(Re-) Expansion initiating temperature (°C)	175	173	174	174	176
Maximum (re-) expanding temperature (°C)	227	227	228	229	227
(Re-) Expansion coefficient (%)	238	207	163	132	104
Running performance of microsphere-filled tire with normal internal pressure	○	○	○	○	○
Running performance of microsphere-filled tire with normal internal pressure at high speed driving	○	○	○	○	○
Running performance of damaged microsphere-filled tire	◎	◎	○	○	○

- 5 As clearly shown in the result in Table 9, the heat-expandable microspheres produced in this Example exhibited superior performance in the evaluations of the running performance with normal internal pressure, the running performance with normal internal pressure at high speed, and the running performance of damaged tire, when they were filled in a tire-and-rim assembly.

[0169] Example C7

- 10 The polymerization was performed in the same manner as in Example C1 except that the oily medium was prepared by mixing 72 g of acrylonitrile, 18 g of methacrylonitrile, 210 g of methacrylic acid, 1.2 g of trimethylolpropane trimethacrylate, 2.0 g of azobisisobutyronitrile, and 150 g of C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>.

- 15 The resultant microspheres had the average particle size of 36 μm, the CV or coefficient of variation of 23 %, the expansion initiating temperature of 188°C, and the maximum expanding temperature of 232°C. The ratio of the blowing agent encapsulated in the heat-expandable microspheres was determined to be 32.7 weight percent. The microspheres did not burn when a source of ignition was brought close to them.

[0170] The resultant heat-expandable microspheres were processed into heat-expanded microspheres

by heating and expanding with the production machine equipped with the expanding device shown in Figure 2. Some of the expanding parameters were controlled constant, 1.0 kg/h for the raw material feeding rate, 0.05 m<sup>3</sup>/min for the flow rate of gas containing dispersed raw material, and 0.5 m<sup>3</sup>/min for the flow rate of hot gas, while the hot gas temperature was controlled into varied levels, 400°C, 450°C, 500°C, 550°C, and 600°C as shown in Table 10. The properties of the resultant heat-expanded microspheres (heat-expandable microspheres) were evaluated and described in Table 10.

[0171] Table 10

	Hot gas temperature				
	400°C	450°C	500°C	550°C	600°C
Sample number	No. 46	No. 47	No. 48	No. 49	No. 50
Average particle size (μm)	89.6	104	126	148	169
Coefficient of variation, CV (%)	23	22	23	23	23
Ratio of encapsulated blowing agent (%)	31.6	31.8	31.7	31.1	30.5
Retention of encapsulated blowing agent (%)	96.6	97.2	96.8	95.2	93.3
True specific gravity (g/cc)	0.079	0.032	0.024	0.017	0.012
Ratio of microspheres having a true specific gravity not lower than 0.79 g/cc (weight percent)	2.1	1.3	0.4	0.7	0.4
Opening of Sieve 1 (μm)/ratio of aggregated microspheres in the screening (weight percent)	175/0	200/0	250/0	300/0	330/0
Opening of Sieve 2 (μm)/ratio of aggregated microspheres in the screening (weight percent)	185/0	215/0	---	---	350/0
Ratio of aggregated microspheres (weight percent)	0	0	0	0	0
(Re-) Expansion initiating temperature (°C)	178	179	178	179	180
Maximum (re-) expanding temperature (°C)	223	223	222	223	225
(Re-) Expansion coefficient (%)	236	218	164	104	101
Running performance of microsphere-filled tire with normal internal pressure	○	○	○	○	○
Running performance of microsphere-filled tire with normal internal pressure at high speed driving	○	○	○	○	○
Running performance of damaged microsphere-filled tire	◎	◎	○	○	○

As clearly shown in the result in Table 10, the heat-expandable microspheres produced in this Example exhibited superior performance in the evaluations of the running performance with normal internal pressure, the running performance with normal internal pressure at high speed, and the running performance of damaged tire, when they were filled in a tire-and-rim assembly.

[0172] Comparative Example C4

The polymerization was performed in the same manner as that in Example C1 except that an oily medium was prepared by mixing 24 g of acrylonitrile, 6.0 g of methacrylonitrile, 270 g of methacrylic acid, 1.2 g of trimethylolpropane trimethacrylate, 2.0 g of azobisisobutyronitrile, and 150 g of C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>.

The resultant microspheres had the average particle size of 31 μm and the CV or coefficient of

variation of 26 %, and did not have expanding performance.

[0173] Example D1

A base paint was prepared by mixing 100 g of polyvinyl chloride (SUMILIT PCX, produced by Sumitomo-Chemical Co., Ltd., with the softening point of 80°C), 100 g of limestone powder (WHITON SB, produced by Shiraishi Calcium Kaisha, Ltd., with the average particle size of 2.2  $\mu\text{m}$ ), 50 g of soft calcium carbonate (light calcium carbonate, produced by Konoshima Chemical Co., Ltd., with the average particle size of 0.3  $\mu\text{m}$ ), 120 g of a plasticizer (SANSO CIZER DINP, a phthalic ester plasticizer, produced by New Japan Chemical Co., Ltd.), and 10 g of a solvent (mineral spirit, produced by Nippon Oil Corporation) with a grain mixer.

A lightweight paint (with a specific gravity of 0.90) was prepared by blending 1.0 g of the heat-expanded microspheres produced in Example B3 and 99 g of the base paint. The heat-expanded microspheres had a re-expanding capacity with the maximum re-expanding temperature of 196°C and the re-expansion coefficient of 180 %. The resultant lightweight paint was subjected to the pressure of 15 MPa at room temperature for the predetermined periods described in Table 11 below, and the specific gravity of the treated lightweight paint was determined. Then the treated lightweight paint was coated on a 7-mm thick iron plate in 2 mm thick coating, and baked at 140°C for 30 minutes in an oven to be processed into coating film, and the specific gravity of the coating film was determined. The baked coating film was baked again at 170°C for 30 minutes in an oven, and the specific gravity of the re-baked coating film was determined. The result is shown in Table 11.

[0174] Table 11

Pressing time (min)	0	30	60	90	120
Specific gravity of pressed paint	0.90	0.91	0.92	0.91	0.93
Specific gravity of baked paint	0.90	0.92	0.94	0.94	0.95
Specific gravity of re-baked paint	0.90	0.92	0.93	0.94	0.94

[0175] Comparative Example D1

A lightweight paint (with the specific gravity of 0.94) was prepared in the same manner as in Example D1, except that the heat-expanded microspheres produced in Comparative Example B3 were blended instead of the heat-expanded microspheres produced in Example B3.

The property of the lightweight paint was determined in the same manner as in Example D1. The result is shown in Table 12.

[0176] Table 12

Pressing time (min)	0	30	60	90	120
Specific gravity of pressed paint	0.94	0.99	1.05	1.16	1.24
Specific gravity of baked paint	0.96	1.03	1.13	1.21	1.28

Specific gravity of re-baked paint	1.10	1.13	1.21	1.27	1.29
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[0177] In Example D1, the specific gravity of the paint hardly changed with the increase of pressing time. On the contrary, in Comparative Example D1, the specific gravity of the paint increased with the increase of pressing time due to the increase of collapsed heat-expanded microspheres by external force. In Example D1, almost no difference was found in the specific gravity between baked coating film and re-baked coating film, and no thermal deflation was observed. On the contrary, in Comparative Example D1, a significant difference was found in the specific gravity between baked coating film and re-baked coating film, and thermal deflation was observed.

#### 10 Industrial Applicability

[0178] The production process for heat-expanded microspheres of the present invention produces heat-expanded microspheres having a particle size distribution with minimum difference in its coefficient of variation before and after heat-expansion and containing slight ratios of aggregated microspheres and microspheres of high true specific gravity.

[0179] The heat-expanded microspheres of the present invention have a property of containing slight ratios of aggregated microspheres and microspheres of high true specific gravity. The heat-expanded microspheres are durable against collapse by external force, and the property enables the heat-expanded microspheres to prevent hardening and shrinking of a porous material composition when they are blended in the composition for lightweight effect, and to solve time-dependent thermal degradation of porous molded products produced from the porous material composition.

[0180] The heat-expandable microsphere A of the present invention are durable against collapse by external force, and the property enables the heat-expandable microspheres to prevent hardening and shrinking of a porous material composition when they are blended in the composition for lightweight effect, and to solve time-dependent thermal degradation of porous molded products produced from the porous material composition.

[0181] The porous molded products of the present invention are produced with sufficient lightweight effect, do not harden or shrink in molding, do not cause time-dependent thermal deflation, and have high dimensional stability.

[0182] The heat-expanded microspheres and heat-expandable microspheres A of the present invention containing a specific fluorine compound as a blowing agent exhibit satisfactory performance for sealing damage on tires and supplying internal pressure to tires, when they are filled in a tire-and-rim assembly as a sealant for damage on tires and an internal pressure supplier for tires.

[0183] The heat-expandable microspheres of the present invention containing a specific fluorine compound as a blowing agent are processed as the raw material for the heat-expanded microspheres and heat-expandable microspheres A, and the microspheres produced from the heat-expandable microspheres exhibit satisfactory performance for sealing damage on tires and supplying internal

pressure to tires, when they are filled in a tire-and-rim assembly as a sealant for damage on tires and an internal pressure supplier for tires. The heat-expandable microspheres attain satisfactory result in the evaluation of not only the tire running performance with normal internal pressure, but also the high-speed tire running performance with normal internal pressure.

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What is claimed is:

1. A method of producing heat-expanded microspheres, which comprises the steps of:  
feeding a gas fluid containing heat-expandable microspheres through a gas-introducing tube  
5 having a dispersion nozzle on its outlet and fixed inside a hot gas flow, and then jetting the gas flow from the dispersion nozzle, wherein each of the heat-expandable microspheres comprises a shell of thermoplastic resin, and a blowing agent encapsulated therein having a boiling point not higher than the softening point of the thermoplastic resin, and have an average particle size from 1 to 100  $\mu\text{m}$ ;  
colliding the gas fluid with a collision plate fixed on a lower portion of the dispersion nozzle  
10 in order to disperse the heat-expandable microspheres in the hot gas flow; and  
heating the dispersed heat-expandable microspheres in the hot gas flow at a temperature not lower than their expansion initiating temperature and thus expanding the heat-expandable microspheres.
- 15 2. A method of producing heat-expanded microspheres according to Claim 1, wherein the gas-introducing tube and/or collision plate is comprised of an overheating prevention function.
3. A method of producing heat-expanded microspheres, comprising the steps of:  
jetting a gas fluid containing heat-expandable microspheres through at least one dispersion  
20 nozzle fixed outside a hot gas flow, and dispersing the gas fluid in the hot gas flow, wherein each of the heat-expandable microspheres comprises a shell of thermoplastic resin, and a blowing agent encapsulated therein having a boiling point not higher than the softening point of the thermoplastic resin, and have an average particle size from 1 to 100  $\mu\text{m}$ ; and  
heating the dispersed heat-expandable microspheres in the hot gas flow at a temperature not  
25 lower than their expansion initiating temperature to thereby expand the heat-expandable microspheres.
4. A method of producing heat-expanded microspheres according to any one of Claims 1 to 3, wherein each of the heat-expandable microspheres further comprises a particulate filler that adheres to  
30 the outer surface of the shell thereof, the particulate filler having an average particle size not greater than one tenth of the average particle size of the heat-expandable microspheres without the particulate filler adhered to the surface thereof.
5. A method of producing heat-expanded microspheres according to any one of Claims 1 to 4,  
35 which further comprises the step of wetting the resultant heat-expanded microspheres with a liquid organic compound which does not dissolve the shells of the heat-expanded microspheres.



6. A method of producing heat-expanded microspheres according to any one of Claims 1 to 5, wherein the expansion conditions of the heat-expandable microspheres are controlled in such a manner that the heat-expanded microspheres do not have a re-expansion initiating temperature.

5 7. A method of producing heat-expanded microspheres according to any one of Claims 1 to 5, wherein the expansion conditions of the heat-expandable microspheres are controlled in such a manner that the heat-expanded microspheres have a re-expansion initiating temperature.

10 8. A method of producing heat-expanded microspheres according to any one of Claims 1 to 7, wherein the blowing agent contains a C<sub>2-10</sub> fluorine compound having an ether structure, and which contains no chlorine and bromine atoms.

15 9. A method of producing heat-expanded microspheres according to Claim 8, wherein the thermoplastic resin is produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group, the weight ratio of the nitrile monomer ranging from 20 to 80 weight percent of the monomer mixture, and the weight ratio of the monomer having a carboxyl group ranging from 80 to 20 weight percent.

20 10. A method of producing heat-expanded microspheres according to Claim 8 or 9, wherein the heat-expandable microspheres further comprise a particulate filler that adheres to the outer surface of the shells thereof, the particulate filler having an average particle size not greater than one tenth of the average particle size of the heat-expandable microspheres without the particulate filler adhered to the surface thereof, and is at least one anti-blocking agent selected from the group consisting of organic compounds having a melting point not lower than 90°C and inorganic compounds having a  
25 layered structure.

30 11. Heat-expanded microspheres produced by a method in which heat-expandable microspheres having an average particle size ranging from 1 to 100 μm, and which each comprise a shell of thermoplastic resin, and a blowing agent having a boiling point not higher than the softening point of the thermoplastic resin and encapsulated in the shell, are heated to a temperature not lower than an expansion initiating temperature of the heat-expandable microspheres to thereby expand the heat-expandable microspheres, wherein the heat-expanded microspheres contain not more than 5 weight percent of aggregated microspheres and not more than 5 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C.

35 12. Heat-expanded microspheres according to Claim 11, wherein the heat-expandable microspheres further comprise a particulate filler that adheres to the outer surface of the shells thereof,

the particulate filler having an average particle size not greater than one tenth of the average particle size of the heat-expandable microspheres without the particulate filler adhered to the surface thereof.

13. Heat-expanded microspheres according to Claim 11 or 12, which are produced by heating and expanding the heat-expandable microspheres, wherein the difference in the coefficient of variation of the particle size distribution between the heat-expanded microspheres and the heat-expandable microspheres is within +/- 5 %.

14. Heat-expanded microspheres according to any one of Claims 11 to 13, which have a re-expansion initiating temperature.

15. Heat-expanded microspheres according to any one of Claims 11 to 14, which are wetted with a liquid organic compound that does not dissolve the shells thereof.

16. Heat-expanded microspheres according to any one of Claims 11 to 15, wherein the blowing agent contains a C<sub>2-10</sub> fluorine compound having an ether structure, and which contains no chlorine and bromine atoms.

17. Heat-expanded microspheres according to Claim 16, wherein the thermoplastic resin is produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group, the weight ratio of the nitrile monomer ranging from 20 to 80 weight percent of the monomer mixture, and the weight ratio of the monomer having a carboxyl group ranging from 80 to 20 weight percent of the monomer mixture.

18. Heat-expanded microspheres according to Claims 16 or 17, wherein the heat-expandable microspheres further comprise a particulate filler that adheres to the outer surface of the shells thereof, the particulate filler having an average particle size not greater than one tenth of the average particle size of the heat-expandable microspheres without the particulate filler adhered to the surface thereof, and is at least one anti-blocking agent selected from the group consisting of organic compounds having a melting point not lower than 90°C and inorganic compounds having a layered structure.

19. Heat-expanded microspheres according to any one of Claims 16 to 18, the heat-expandable microspheres exhibiting a damage sealing function and a tire internal pressure supply function after a tire is damaged by filling the heat-expanded microspheres in a cavity of a tire-and-rim assembly.

20. Heat-expanded microspheres according to any one of Claims 11 to 19, which are

produced by the process according to any one of Claims 1 to 10.

21. Heat-expandable microspheres, comprising:

a shell of thermoplastic resin, and a blowing agent having a boiling point not higher than the softening point of the thermoplastic resin and encapsulated in the shell;

wherein the heat-expandable microspheres have an average particle size ranging from 1 to 1000  $\mu\text{m}$ ;

an expansion coefficient over 100 % at their maximum expanding temperature, contain not more than 5 weight percent of aggregated microspheres; and

contain not more than 5 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C.

22. Heat-expandable microspheres according to Claim 21, which further comprise a particulate filler that adheres to the outer surface of the shells thereof and has an average particle size not greater than 10  $\mu\text{m}$ .

23. Heat-expandable microspheres according to Claim 21 or 22, which contain not more than 1 weight percent of aggregated microspheres and not more than 3 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C.

24. Heat-expandable microspheres according to any one of Claims 21 to 23, which are wetted with a liquid organic compound that does not dissolve the shells thereof.

25. Heat-expandable microspheres according to any one of Claims 21 to 24, wherein the blowing agent contains a  $\text{C}_{2-10}$  fluorine compound having an ether structure, and which contains no chlorine and bromine atoms.

26. Heat-expandable microspheres according to Claim 25, wherein the coefficient of variation of the particle size distribution thereof is not greater than 30 %.

27. Heat-expandable microspheres according to Claims 25 or 26, wherein the thermoplastic resin is produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group, the weight ratio of the nitrile monomer ranging from 20 to 80 weight percent of the monomer mixture, and the weight ratio of the monomer having a carboxyl group ranging from 80 to 20 weight percent of the monomer mixture.

28. Heat-expandable microspheres according to any one of Claims 25 to 27, further

comprising a particulate filler that adheres to the outer surface of the shell, the particulate filler having an average particle size not greater than 10  $\mu\text{m}$ , and is at least one selected from the group consisting of organic compounds having a melting point not lower than 90°C and inorganic compounds having a layered structure.

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29. Heat-expandable microspheres according to any one of Claims 25 to 28, the heat-expandable microspheres exhibiting a damage sealing function and a tire internal pressure supply function after a tire is damaged by filling the heat-expanded microspheres in a cavity of a tire-and-rim assembly.

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30. A porous material composition, which comprises a base component, and heat-expanded microspheres according to any one of Claims 11 to 20 and/or heat-expandable microspheres according to any one of Claims 21 to 29.

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31. A porous molded product produced by molding a porous material composition according to Claim 30.

32. Heat-expandable microspheres, comprising:

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a shell of thermoplastic resin, and a blowing agent having a boiling point not higher than the softening point of the thermoplastic resin, the heat-expandable microspheres having an average particle size ranging from 1 to 100  $\mu\text{m}$ ;

wherein the blowing agent contains a  $\text{C}_{2-10}$  fluorine compound having an ether structure, and which contains no chlorine and bromine atoms; and

25

wherein the thermoplastic resin is produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group, the weight ratio of the nitrile monomer ranges from 20 to 80 weight percent of the monomer mixture, and the weight ratio of the monomer having a carboxyl group ranges from 80 to 20 weight percent of the monomer mixture.

33. Heat-expandable microspheres, comprising:

30

a shell of thermoplastic resin, a blowing agent having a boiling point not higher than the softening point of the thermoplastic resin and encapsulated in the shell, and an anti-blocking agent that adheres to the outer surface of the shell, the heat-expandable microspheres having an average particle size ranging from 1 to 100  $\mu\text{m}$ ;

35

wherein the blowing agent contains a  $\text{C}_{2-10}$  fluorine compound having an ether structure, and which contains no chlorine and bromine atoms;

wherein the thermoplastic resin is produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group, the weight ratio of the

nitrile monomer ranging from 20 to 80 weight percent of the monomer mixture, and the weight ratio of the monomer having a carboxyl group ranging from 80 to 20 weight percent; and

wherein the anti-blocking agent is at least one selected from the group consisting of organic compounds having a melting point not lower than 90°C and inorganic compounds having a layered structure.

34. Heat-expandable microspheres, comprising:

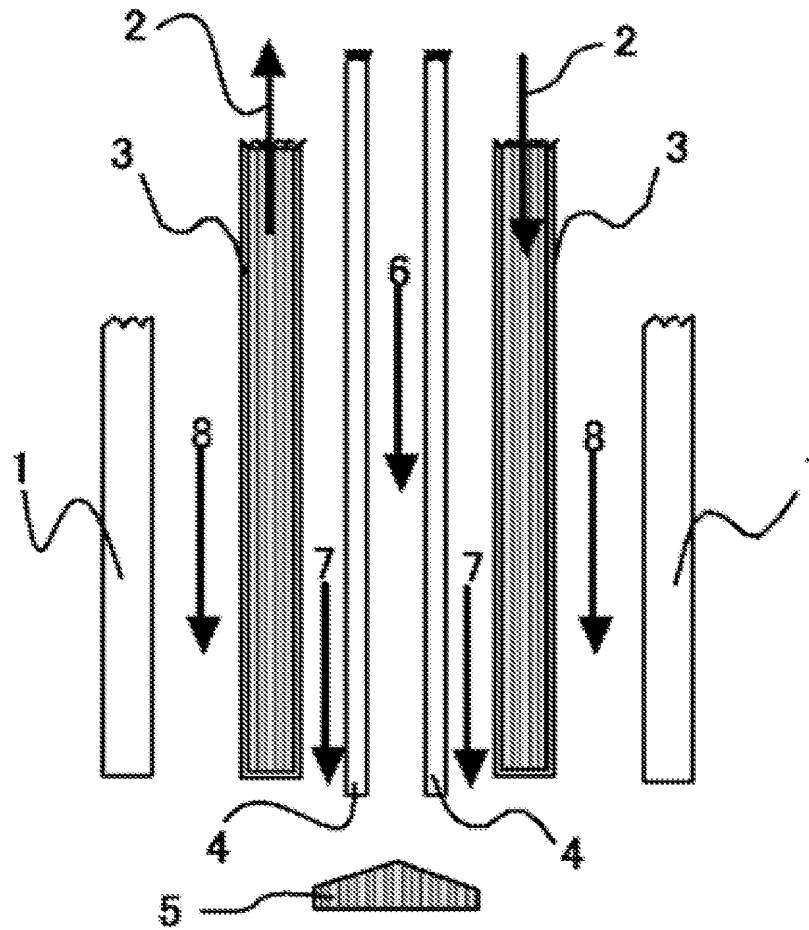
a shell of thermoplastic resin, a blowing agent having a boiling point not higher than the softening point of the thermoplastic resin and encapsulated in the shell, and an anti-blocking agent that adheres to the outer surface of the shell, the heat-expandable microspheres having an average particle size ranging from 1 to 100 μm;

wherein the blowing agent contains a C<sub>2-10</sub> fluorine compound having an ether structure and which contains no chlorine and bromine atoms, and the anti-blocking agent is at least one selected from the group consisting of organic compounds having a melting point not lower than 90°C and inorganic compounds having a layered structure.

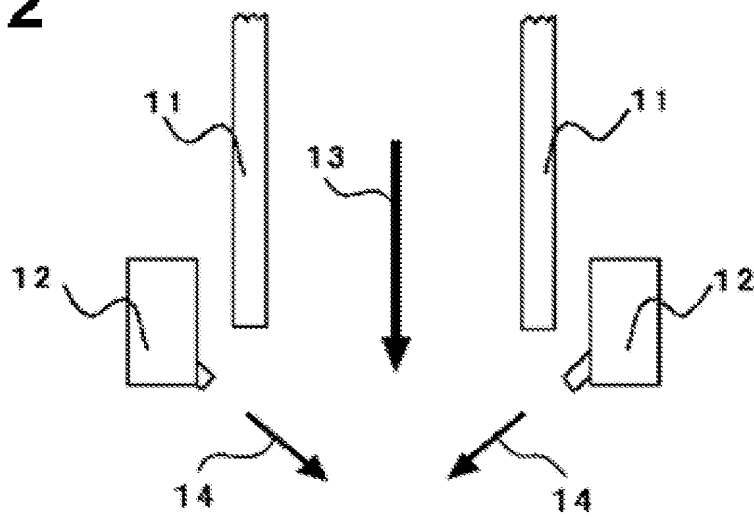
## ABSTRACT

A production process for heat-expanded microspheres comprising the step of providing a gaseous  
5 fluid containing heat-expandable microspheres, which comprise shell of thermoplastic resin and a  
blowing agent encapsulated therein having a boiling point not higher than the softening point of the  
thermoplastic resin and have an average particle size from 1 to 100  $\mu\text{m}$ , feeding the gaseous fluid  
through a gas-introducing tube having a dispersion nozzle on its outlet and being fixed inside a hot  
gas flow, and emitting a jet of the gaseous fluid through the dispersion nozzle; a step wherein the  
10 gaseous fluid is collided on a collision plate fixed under the dispersion nozzle so as to disperse the  
heat-expandable microspheres in the hot gas flow; and a step wherein the dispersed heat-expandable  
microspheres are heated in the hot gas flow at a temperature not lower than their expansion initiating  
temperature and thus expanded. The production process results in minimum difference in the  
variation coefficient of particle size distribution between the microspheres before and after  
15 heat-expansion, slight ratio of raw microspheres and slightly expanded microspheres contained in  
resultant heat-expanded microspheres, and suppressed formation of aggregated microspheres.

**Fig. 1**



**Fig. 2**



## 特許協力条約に基づく国際出願願書

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0-7	出願人又は代理人の書類記号	MMYWO041113P
I	発明の名称	熱膨張した微小球、その製造方法、熱膨張性微小球および用途
II	出願人	
II-1	この欄に記載した者は	出願人である (applicant only)
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II-8	電話番号	0729-91-1001
II-9	ファクシミリ番号	0729-94-8812
II-11	出願人登録番号	000188951



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III-1-7	住所(国名)	
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III-4-6	国籍(国名)	日本国 JP
III-4-7	住所(国名)	日本国 JP

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III-5-5ja	あて名	5810075 日本国 大阪府八尾市渋川町2丁目1-3 松本油脂製薬株式会社内
III-5-5en	Address:	c/o MATSUMOTO YUSHI-SEIYAKU CO., LTD. 1-3, Shibukawa-cho, 2-chome, Yao-shi, OSAKA 581-0075 Osaka 5810075 Japan
III-5-6	国籍(国名)	日本国 JP
III-5-7	住所(国名)	日本国 JP
IV-1	代理人又は共通の代表者、通知のあて名 下記の者は国際機関において右記のごとく 出願人のために行動する。	代理人 (agent)
IV-1-1ja	氏名(姓名)	小野 由己男
IV-1-1en	Name (LAST, First):	ONO, Yukio
IV-1-2ja	あて名	5300054 日本国 大阪府大阪市北区南森町1丁目4番19号 サウスホ レストビル 新樹グローバル・アイピー特許業務法人
IV-1-2en	Address:	SHINJYU GLOBAL IP South Forest Bldg., 1-4-19, Minamimori-machi, Kita-ku, Osaka-shi, Osaka 530-0054 Osaka 5300054 Japan
IV-1-3	電話番号	06-6316-5533
IV-1-4	ファクシミリ番号	06-6316-5544
IV-1-5	電子メール	mailosaka@giplaw.com
IV-1-6	代理人登録番号	100094145
IV-2	その他の代理人	筆頭代理人と同じあて名を有する代理人 (additional agent(s) with the same address as first named agent)
IV-2-1ja	氏名	堀川 かおり(100117422); 門脇 学(100125128)
IV-2-1en	Name(s)	HORIKAWA, Kaori(100117422); KADOWAKI, Manabu(100125128)
V	国の指定	
V-1	この願書を用いてされた国際出願は、規則 4.9(a)に基づき、国際出願の時点で拘束さ れる全てのPCT締約国を指定し、取得しう あらゆる種類の保護を求め、及び該当する 場合には広域と国内特許の両方を求める 国際出願となる。	

## 特許協力条約に基づく国際出願願書

紙面による写し(注意:電子データが原本となります)

VI-1	先の国内出願に基づく優先権主張		
VI-1-1	出願日	2003年 11月 19日 (19. 11. 2003)	
VI-1-2	出願番号	2003-428337	
VI-1-3	国名	日本国 JP	
VI-2	先の国内出願に基づく優先権主張		
VI-2-1	出願日	2003年 11月 20日 (20. 11. 2003)	
VI-2-2	出願番号	2003-431301	
VI-2-3	国名	日本国 JP	
VI-3	先の国内出願に基づく優先権主張		
VI-3-1	出願日	2004年 08月 24日 (24. 08. 2004)	
VI-3-2	出願番号	2004-274187	
VI-3-3	国名	日本国 JP	
VI-4	優先権証明書送付の請求 上記の先の出願のうち、右記の番号のものについては、出願書類の認証謄本を作成し国際事務局へ送付することを、受理官庁に対して請求している。	VI-1, VI-2, VI-3	
VII-1	特定された国際調査機関(ISA)	日本国特許庁 (ISA/JP)	
VIII	申立て	申立て数	
VIII-1	発明者の特定に関する申立て	—	
VIII-2	出願し及び特許を与えられる国際出願日における出願人の資格に関する申立て	—	
VIII-3	先の出願の優先権を主張する国際出願日における出願人の資格に関する申立て	—	
VIII-4	発明者である旨の申立て(米国を指定国とする場合)	—	
VIII-5	不利にならない開示又は新規性喪失の例外に関する申立て	—	
IX	照合欄	用紙の枚数	添付された電子データ
IX-1	願書(申立てを含む)	6	✓
IX-2	明細書	52	✓
IX-3	請求の範囲	6	✓
IX-4	要約	1	✓
IX-5	図面	1	✓
IX-7	合計	66	
	添付書類	添付	添付された電子データ
IX-8	手数料計算用紙	—	✓
IX-17	PCT-SAFE 電子出願	—	—
IX-19	要約書とともに提示する図の番号		
IX-20	国際出願の使用言語名	日本語	
X-1	出願人、代理人又は代表者の記名押印	/100094145/	
X-1-1	氏名(姓名)	小野 由己男	
X-1-2	署名者の氏名		
X-1-3	権限		

## 特許協力条約に基づく国際出願願書

紙面による写し(注意:電子データが原本となります)

## 受理官庁記入欄

10-1	国際出願として提出された書類の実際の受理の日	
10-2	図面	
10-2-1	受理された	
10-2-2	不足図面がある	
10-3	国際出願として提出された書類を補完する書類又は図面であってその後期間内に提出されたものの実際の受理の日(訂正日)	
10-4	特許協力条約第11条(2)に基づく必要な補完の期間内の受理の日	
10-5	出願人により特定された国際調査機関	ISA/JP
10-6	調査手数料未払いにつき、国際調査機関に調査用写しを送付していない	

## 国際事務局記入欄

11-1	記録原本の受理の日	
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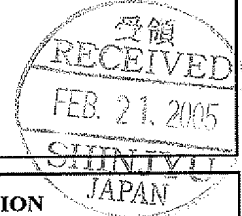
From the INTERNATIONAL BUREAU

**PCT**NOTIFICATION CONCERNING  
SUBMISSION OR TRANSMITTAL  
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

ONO, Yukio  
SHINJYU GLOBAL IP South Forest Bldg., 1-4-19,  
Minamimori-machi, Kita-ku, Osaka-shi, Osaka 530-0054 Osaka  
5300054  
JAPON



Date of mailing (day/month/year) 09 February 2005 (09.02.2005)	
Applicant's or agent's file reference MMYWO041113P	<b>IMPORTANT NOTIFICATION</b>
International application No. PCT/JP04/016940	International filing date (day/month/year) 15 November 2004 (15.11.2004)
International publication date (day/month/year)	Priority date (day/month/year) 19 November 2003 (19.11.2003)
Applicant MATSUMOTO YUSHI-SEIYAKU CO., LTD. et al	

- By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- (If applicable)* The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- (If applicable)* An asterisk (\*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b) (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
19 November 2003 (19.11.2003)	2003-428337	JP	20 January 2005 (20.01.2005)
20 November 2003 (20.11.2003)	2003-431301	JP	20 January 2005 (20.01.2005)
24 August 2004 (24.08.2004)	2004-274187	JP	20 January 2005 (20.01.2005)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland  Facsimile No. +41 22 740 14 35	Authorized officer  <b>Akreml Taieb</b>  Facsimile No. +41 22 338 90 90 Telephone No. +41 22 338 9415
---	--

From the INTERNATIONAL BUREAU

**PCT**NOTIFICATION CONCERNING  
SUBMISSION OR TRANSMITTAL  
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

ONO, Yukio  
SHINJYU GLOBAL IP South Forest Bldg., 1-4-19,  
Minamimori-machi, Kita-ku, Osaka-shi, Osaka 530-0054 Osaka  
5300054  
JAPON

Date of mailing (day/month/year) 09 February 2005 (09.02.2005)	
Applicant's or agent's file reference MMYWO041113P	<b>IMPORTANT NOTIFICATION</b>
International application No. PCT/JP04/016940	International filing date (day/month/year) 15 November 2004 (15.11.2004)
International publication date (day/month/year)	Priority date (day/month/year) 19 November 2003 (19.11.2003)
Applicant MATSUMOTO YUSHI-SEIYAKU CO., LTD. et al	

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Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
19 November 2003 (19.11.2003)	2003-428337	JP	20 January 2005 (20.01.2005)
20 November 2003 (20.11.2003)	2003-431301	JP	20 January 2005 (20.01.2005)

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Authorized officer

Akremi Taieb

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Telephone No. +41 22 338 9415



PCT

NOTIFICATION CONCERNING  
SUBMISSION OR TRANSMITTAL  
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To:

ONO, Yukio  
SHINJYU GLOBAL IP South Forest Bldg., 1-4-19,  
Minamimori-machi, Kita-ku, Osaka-shi, Osaka 530-0054 Osaka  
5300054  
JAPON

Date of mailing (day/month/year) 09 February 2005 (09.02.2005)	
Applicant's or agent's file reference MMYWO041113P	IMPORTANT NOTIFICATION
International application No. PCT/JP04/016940	International filing date (day/month/year) 15 November 2004 (15.11.2004)
International publication date (day/month/year)	Priority date (day/month/year) 19 November 2003 (19.11.2003)
Applicant MATSUMOTO YUSHI-SEIYAKU CO., LTD. et al	

- By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
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Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
19 November 2003 (19.11.2003)	2003-428337	JP	20 January 2005 (20.01.2005)

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Authorized officer

Akremi Taieb

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Telephone No. +41 22 338 9415



From the INTERNATIONAL BUREAU

**PCT**

SECOND AND SUPPLEMENTARY NOTICE  
INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION (TO DESIGNATED OFFICES  
WHICH APPLY THE 30 MONTH TIME  
LIMIT UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To:

ONO, Yukio  
SHINJYU GLOBAL IP South Forest Bldg., 1-4-19,  
Minamimori-machi, Kita-ku, Osaka-shi, Osaka  
530-0054  
JAPON

Date of mailing (day/month/year)

23 March 2006 (23.03.2006)

Applicant's or agent's file reference

MMYWO041113P

**IMPORTANT NOTICE**

International application No.

PCT/JP2004/016940

International filing date (day/month/year)

15 November 2004 (15.11.2004)

Priority date (day/month/year)

19 November 2003 (19.11.2003)

Applicant

MATSUMOTO YUSHI-SEIYAKU CO., LTD. et al

- ATTENTION:** For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does not apply**, please see Form PCT/IB/308(First Notice) issued previously.
- Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93bis.1. The International Bureau has effected that communication on the date indicated below:  
02 June 2005 (02.06.2005)

AU, AZ, BY, CN, CO, DZ, EP, HU, KG, KP, KR, MD, MK, MZ, NA, PG, RU, SY, TM, US

In accordance with Rule 47.1(c-bis)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

- The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93bis.1:

AE, AG, AL, AM, AP, AT, BA, BB, BG, BR, BW, BZ, CA, CR, CU, CZ, DE, DK, DM, EA, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, ID, IL, IN, IS, JP, KE, KZ, LC, LK, LR, LS, LT, LV, MA, MG, MN, MW, MX, NI, NO, NZ, OA, OM, PH, PL, PT, RO, SC, SD, SG, SK, SL, TJ, TN, TR, TT, UA, UZ, VC, VN, YU, ZA, ZW

In accordance with Rule 47.1(c-bis)(ii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application.

**4. TIME LIMITS for entry into the national phase**

For the designated or elected Office(s) listed above, the applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **30 MONTHS** from the priority date.

In practice, **time limits other than the 30-month time limit** will continue to apply, for various periods of time, in respect of certain of the designated or elected Office(s) listed above. For **regular updates on the applicable time limits** (30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/index.html>.

It is the applicant's **sole responsibility** to monitor all these time limits.



The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Authorized officer

Yoshiko Kuwahara

Facsimile No.+41 22 740 14 35

Facsimile No.+41 22 338 90 90

(19) 世界知的所有権機関  
国際事務局(43) 国際公開日  
2005 年 6 月 2 日 (02.06.2005)

PCT

(10) 国際公開番号  
WO 2005/049698 A1

(51) 国際特許分類: C08J 3/12, 9/32, C09K 3/00

(21) 国際出願番号: PCT/JP2004/016940

(22) 国際出願日: 2004 年 11 月 15 日 (15.11.2004)

(25) 国際出願の言語: 日本語

(26) 国際公開の言語: 日本語

(30) 優先権データ:  
特願 2003-428337 2003 年 11 月 19 日 (19.11.2003) JP  
特願 2003-431301 2003 年 11 月 20 日 (20.11.2003) JP  
特願 2004-274187 2004 年 8 月 24 日 (24.08.2004) JP

(71) 出願人 (米国を除く全ての指定国について): 松本油脂製薬株式会社 (MATSUMOTO YUSHI-SEIYAKU CO., LTD.) [JP/JP]; 〒5810075 大阪府八尾市渋川町 2 丁目 1 番 3 号 Osaka (JP).

(72) 発明者; および

(75) 発明者/出願人 (米国についてのみ): 増田 俊明 (MA-SUDA, Toshiaki) [JP/JP]; 〒5810075 大阪府八尾市渋川町 2 丁目 1-3 松本油脂製薬株式会社内 Osaka (JP). 藤江 孝司 (FUJIE, Takashi) [JP/JP]; 〒5810075 大阪府八尾市渋川町 2 丁目 1-3 松本油脂製薬株式会社内 Osaka (JP). 高原 一郎 (TAKAHARA, Ichiro) [JP/JP]; 〒5810075 大阪府八尾市渋川町 2 丁目 1-3 松本油脂製薬株式会社内 Osaka (JP). 寄嶋 郁雄 (YOSEJIMA, Ikuo) [JP/JP]; 〒5810075 大阪府八尾市渋川町 2 丁目 1-3 松本油脂製薬株式会社内 Osaka (JP). 三木 勝志

(MIKI, Katsushi) [JP/JP]; 〒5810075 大阪府八尾市渋川町 2 丁目 1-3 松本油脂製薬株式会社内 Osaka (JP).

(74) 代理人: 小野 由己男, 外 (ONO, Yukio et al.); 〒5300054 大阪府大阪市北区南森町 1 丁目 4 番 1 9 号 サウスホレストビル 新樹グローバル・アイビー特許業務法人 Osaka (JP).

(81) 指定国 (表示のない限り、全ての種類の国内保護が可能): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) 指定国 (表示のない限り、全ての種類の広域保護が可能): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), ユーラシア (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), ヨーロッパ (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

添付公開書類:  
— 国際調査報告書

2 文字コード及び他の略語については、定期発行される各 PCT ガゼットの巻頭に掲載されている「コードと略語のガイダンスノート」を参照。

(54) Title: THERMALLY EXPANDED MICROSPHERE, PROCESS FOR PRODUCING THE SAME, THERMALLY EXPANDABLE MICROSPHERE AND USE THEREOF

(54) 発明の名称: 熱膨張した微小球、その製造方法、熱膨張性微小球および用途

(57) Abstract: A process for producing thermally expanded microspheres, comprising the step of providing a gaseous fluid carrying thermally expandable microspheres of 1 to 100  $\mu$ m average particle diameter composed of an outer shell of thermoplastic resin and, enclosed therein, a blowing agent having a boiling point not higher than the softening point of the thermoplastic resin, passing the gaseous fluid through a gas introduction pipe fitted at its outlet with a dispersion nozzle and disposed inside a hot air stream, and emitting a jet of the gaseous fluid from the dispersion nozzle; the step of causing the gaseous fluid to collide with a collision board disposed at a lower part of the dispersion nozzle so as to disperse thermally expanded microspheres in the hot air stream; and the step of heating the dispersed thermally expanded microspheres at expansion initiation temperature or higher in the hot air stream to thereby attain expansion. In this process, the change of variation coefficient of particle size distribution brought about by thermally expansion is trivial. Further, the amount of raw material and slightly expanded microspheres is less, and the agglomeration of microspheres is suppressed.(57) 要約: 熱膨張した微小球の製造方法は、熱可塑性樹脂からなる外殻と、それに内包され且つ前記熱可塑性樹脂の軟化点以下の沸点を有する発泡剤とから構成され、平均粒子径が 1 ~ 100  $\mu$ m である熱膨張性微小球を含む気体流体を、出口に分散ノズルを備え且つ熱風流の内側に設置された気体導入管に流し、前記分散ノズルから噴射させる工程と、前記気体流体を前記分散ノズルの下部に設置された衝突板に衝突させ、熱膨張性微小球を前記熱風流中に分散させる工程と、分散した熱膨張性微小球を前記熱風流中で膨張開始温度以上に加熱して膨張させる工程とを含む製造方法である。この製造方法では、熱膨張前後での粒度分布の変動係数の変化が小さく、原料やわずかに膨張した微小球の量が少なく、凝集微小球の生成が抑制される。

WO 2005/049698 A1

## 明 細 書

### 熱膨張した微小球、その製造方法、熱膨張性微小球および用途 技術分野

- [0001] 本発明は、熱膨張した微小球、その製造方法、熱膨張性微小球および用途に関する。さらに詳しくは、本発明は、熱膨張前後において粒度分布の変動係数の変化が少なく、凝集微小球や真比重の大きな微小球（所望の熱膨張ができなかった微小球）の含有率が極めて低い熱膨張した微小球およびその製造方法と、凝集微小球や真比重の大きな微小球の含有率が極めて低く、外力で破損しにくく、軽量化を目的とした中空体組成物の成形時に硬化収縮を防止でき、経時的な熱ヘタリの問題を解消できる熱膨張性微小球と、これらの微小球の用途に関する。
- [0002] 本発明において、特定の含弗素化合物を内包する熱膨張性微小球および熱膨張した微小球は、タイヤとリムとの組立体の空洞部分に充填されて、タイヤ受傷時に優れた受傷部封止材、タイヤ内圧付与材として使用される。

### 背景技術

- [0003] 熱可塑性樹脂を外殻とし、その内部に発泡剤が封入された構造を有する熱膨張性微小球は、一般に熱膨張性マイクロカプセルと呼ばれている。熱可塑性樹脂としては、通常、塩化ビニリデン系共重合体、アクリロニトリル系共重合体、アクリル系共重合体等が用いられている。また、発泡剤としてはイソブタンやイソペンタン等の炭化水素が主に使用されている（特許文献1参照）。
- [0004] このような熱膨張性マイクロカプセルを加熱膨張させることによって、軽量な中空微粒子（熱膨張した微小球）が得られる。熱膨張性マイクロカプセルを膨張させる方法として、熱膨張性マイクロカプセルの分散液を加熱空気中に噴霧して膨張と乾燥を同時に行う方法が提案されている（特許文献2参照）。しかし、使用した分散機の先端に凝集体が生成する可能性が高く問題がある。

また、発泡剤を含浸させて得られる熱膨張マイクロカプセルを電気式熱風発生機による熱風で膨張させて、中空微粒子を得る方法が提案されている（特許文献3参照）。その比較例3に記載されているように、発泡剤を内包した熱膨張マイクロカプセルに

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/016940

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl<sup>7</sup> C08J3/12, C08J9/32, C09K3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl<sup>7</sup> B01J13/02, C08J3/12, C08J9/32, C09K3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-2004	Toroku Jitsuyo Shinan Koho	1994-2004
Kokai Jitsuyo Shinan Koho	1971-2004	Jitsuyo Shinan Toroku Koho	1996-2004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-151895 A (Matsumoto Yushi-Seiyaku Co., Ltd.), 05 June, 2001 (05.06.01), Claim 1 (Family: none)	1-34
A	EP 1288727 A1 (KUREHA KAGAKU KOGYO KABUSHIKI KAISHA), 05 March, 2003 (05.03.03), Claims 1, 5, 8; Par. Nos. [0030] to [0032] & JP 2002-12693 A Claims 1, 5, 8; Par. No. [0019] & WO 01/83636 A1 & US 2003/114546 A1 & US 2003/143399 A1	1-34

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search  
10 December, 2004 (10.12.04)

Date of mailing of the international search report  
28 December, 2004 (28.12.04)

Name and mailing address of the ISA/  
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/JP2004/016940

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-269343 A (Inoac Corp.), 05 October, 1999 (05.10.99), Claim 2 (Family: none)	32-34
P,A	WO 2004/74396 A1 (Matsumoto Yushi-Seiyaku Co., Ltd.), 02 September, 2004 (02.09.04), Claims 1 to 5 (Family: none)	32-34

## A. 発明の属する分野の分類 (国際特許分類 (IPC))

Int. C1<sup>7</sup> C08J 3/12、C08J 9/32、C09K 3/00

## B. 調査を行った分野

## 調査を行った最小限資料 (国際特許分類 (IPC))

Int. C1<sup>7</sup> B01J 13/02、C08J 3/12、C08J 9/32、C09K 3/00

## 最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報 1926-2004年

日本国公開実用新案公報 1971-2004年

日本国登録実用新案公報 1994-2004年

日本国実用新案登録公報 1996-2004年

## 国際調査で使用した電子データベース (データベースの名称、調査に使用した用語)

## C. 関連すると認められる文献

引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
A	JP 2001-151895 A (松本油脂製薬株式会社) 2001.06.05、【請求項1】 (ファミリーなし)	1-34
A	EP 1288727 A1 (KUREHA KAGAKU KOGYO KABUSHIKI KA ISYA) 2003.03.05、請求項1、請求項5、請求項8、段 落 [0030] - [0032] & JP 2002-12693 A、【請求項1】、【請求項 5】、【請求項8】、段落【0019】 & WO 01/83636 A1	1-34

☒ C欄の続きにも文献が列挙されている。☐ パテントファミリーに関する別紙を参照。

## \* 引用文献のカテゴリー

「A」 特に関連のある文献ではなく、一般的技術水準を示すもの

「E」 国際出願日前の出願または特許であるが、国際出願日以後に公表されたもの

「L」 優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献 (理由を付す)

「O」 口頭による開示、使用、展示等に言及する文献

「P」 国際出願日前で、かつ優先権の主張の基礎となる出願

の日の後に公表された文献

「T」 国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの

「X」 特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの

「Y」 特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの

「&amp;」 同一パテントファミリー文献

国際調査を完了した日

10.12.2004

国際調査報告の発送日

28.12.2004

国際調査機関の名称及びあて先

日本国特許庁 (ISA/JP)

郵便番号100-8915

東京都千代田区霞が関三丁目4番3号

特許庁審査官 (権限のある職員)

森川 聡

4 J

9268

電話番号 03-3581-1101 内線 3456

C (続き) . 関連すると認められる文献		
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
A	&US 2003/114546 A1 &US 2003/143399 A1	
	JP 11-269343 A (株式会社イノアックコーポレーション) 1999. 10. 05、【請求項2】 (ファミリーなし)	32-34
PA	WO 2004/74396 A1 (松本油脂製菓株式会社) 2004. 09. 02、請求項1-5 (ファミリーなし)	32-34

## AMENDMENT IN THE INTERNATIONAL PHASE UNDER ARTICLE 11 PCT

To: Examiner of the Japanese Patent Office

1. International Application Number      PCT/JP2004/16940

2. Applicant

Name	Matsumoto Yushi-Seiyaku Co., Ltd.
Address	1-3, Shibukawa-cho 2-choume, Yao-shi, Osaka Prefecture, 581-0075 JAPAN
Nation	Japan
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3. Attorney

Name	(9414) ONO Yukio
Address	South Forest Bldg., 1-4-19, Minamimori-machi, Kita-ku, Osaka City, Osaka 530-0054 JAPAN

4. Subject of the Amendment      Specification and Claims

5. Content of the Amendment

- (1) Please amend "heat-expanding microspheres" at page 1, line 25 of the specification as "heat-expandable microspheres".
- (2) Please amend "whose internal pressure decreased" at page 5, line 25 as of the specification "in which internal pressure has decreased".
- (3) Please amend "under the dispersion nozzle" at starting at page 6, line 16-17 of the specification as "on a downstream portion of the dispersion nozzle".
- (4) Please amend "pentaerythrutol tri(meth)acrylate" at page 12, line 11 and line 12 of the specification as "pentaerythritol tri(meth)acrylate,."
- (5) Please amend "dipentaerythrutol hexaacrylate" at page 12, line 12 and line 13 of the specification as "dipentaerythritol hexaacrylate".
- (6) Please amend "di-3-methoxybutyl peroxy dicarbonate 3,5,5-trimethyl hexanoyl peroxide" at page 13, line 5 and line 6 of the specification as "di-3-methoxybutyl peroxy dicarbonate, 3,5,5-trimethyl hexanoyl peroxide".
- (7) Please amend "As dispersion-stabilizing auxiliaries" at page 13, line 22 and line 23 of the specification as "As dispersion-stabilizing auxiliaries,".
- (8) Please amend "New-Gram Machine (manufactured by Seishin Enterprise Co., Ltd.)" at page 17, line 1 and line 2 of the specification as "New-Gra Machine (manufactured by Seishin Enterprise Co., Ltd.)".
- (9) Please amend "on the lower portion of the dispersion nozzle" at page 17, line 12 of the specification as "on a downstream portion of the dispersion nozzle".
- (10) Please amend "on the lower portion of the dispersion nozzle" at page 17, line 19 of the specification as "on a downstream portion of the dispersion nozzle".
- (11) Please amend "to improve the dispersion of heat-expandable microspheres" at page 17, line 23 of the specification as "for improving the dispersion of heat-expandable microspheres".
- (12) Please amend "running performance in high-speed driving with normal pressure" at page 23, line 23 of the specification as "running performance in driving with normal pressure".
- (13) Please amend "the gas fluid ..... on a lower portion of the dispersion nozzle" in



the claim 1 at page 53 of the Claims as “the gas fluid ..... on a downstream side of the dispersion nozzle”.

7. List of the Items Filed Herewith

- (1) Pages 1, 5, 6, 12, 13, 17 and 23 of the Specification
- (2) Page 53 of the Claims

## DESCRIPTION

### THERMALLY EXPANDED MICROSPHERE, PROCESS FOR PRODUCING THE SAME, THERMALLY EXPANDABLE MICROSPHERE AND USE THEREOF

#### Technical Field

[0001] The present invention relates to heat-expanded microspheres, a production process thereof, heat-expandable microspheres, and application thereof. More specifically, the present invention relates to heat-expanded microspheres, which have a particle size distribution with a coefficient of variation showing a minimum difference before and after heat expansion, and which contain slight ratios of aggregated microspheres and microspheres of high true specific gravity (microspheres not having been expanded to a prescribed degree); a production process thereof; heat-expandable microspheres, which contain slight ratios of aggregated microspheres and microspheres of high true specific gravity, are resistant to damage from external force, prevent the hardening and shrinkage of porous material compositions for weight reduction in molding processes, and solve the problem of time-dependent thermal deflation; and the application thereof.

[0002] In the present invention, the heat-expandable and heat-expanded microspheres in which a specific fluorine compound is encapsulated, are filled in a cavity of a tire-and-rim assembly, as a superior sealing material and internal pressure supplier when the tire is damaged.

#### Technical Background

[0003] Heat-expandable microspheres comprising a structure of a shell of thermoplastic resin and a blowing agent encapsulated therein are generally called heat-expandable microcapsules. Vinylidene chloride copolymers, acrylonitrile copolymers, and acrylic copolymers are usually employed as the thermoplastic resin, and hydrocarbons, such as isobutane and isopentane, are mostly employed as the blowing agent. (Refer to Patent Literature 1.)

[0004] Such heat-expandable microcapsules are processed into lightweight hollow particles (heat-expanded microspheres) with heating and expanding. A process for spraying a dispersion of heat-expandable microcapsules in hot gas to expand and dry the microcapsules simultaneously has been proposed as a process for expanding heat-expandable microcapsules. (Refer to Patent Literature 2.) The process, however, has a problem, in that the deposition of aggregated microcapsules at the end of the spray used is highly likely.

A process for producing hollow particulates by expanding heat-expandable microcapsules, which have been produced by impregnating the same with a blowing agent, in hot gas from an electric hot gas generator has been proposed. (Refer to Patent Literature 3.) As described in comparative example 3 in Patent Literature 3, the process completely failed to produce particulates having preferable properties, when the process was applied to expand heat-expanding microcapsules in which

(3) The heat-expanded microspheres that are capable of re-expanding produced in the above (2) are also novel heat-expandable microspheres having properties which were not found in the past.

(4) In a porous material composition containing the heat-expanded microspheres having a capacity of re-expanding in the above (2) and/or the heat-expandable microspheres in the above (3), the microspheres have comparatively thick shells and are durable against rupture under external force. Those microspheres prevent hardening and shrinking of the composition in molding, prevent time-dependent thermal deflation of products at high temperature, and attain superior dimensional stability owing to their optimum heat-expanding property, etc.

[0020] The inventors have also obtained the findings on heat-expandable microspheres and heat-expanded microspheres containing a specific fluorine compound as a blowing agent as described in the following (5) to (8).

[0021] (5) A fluorine compound is preferable for its flame-retardant properties. The heat-expanded microspheres produced by heating and expanding heat-expandable microspheres in this specific process made a damaged tire runnable after its internal pressure has decreased due to damage, when the expanded microspheres were filled in a tire-and-rim assembly to test the applicability of the microspheres for running damaged tires.

(6) Heat-expanded microspheres that are capable of re-expanding and produced by controlling the expansion of heat-expandable microspheres, can be filled in a tire-and-rim assembly for running a damaged tire in which internal pressure has decreased, similar to heat-expanded microspheres produced by expanding heat-expandable microspheres almost completely in the specific process. It is preferable for the heat-expanded microspheres that are capable of re-expanding, in particular, to have the ability to start re-expanding at a prescribed high temperature. Recently, tires are required to run normally even at high temperatures. It is also required that tires have the ability to supply internal pressure by re-expanding immediately after the tire is damaged and its internal pressure has decreased.

[0022] (7) Heat-expanded microspheres that are capable of re-expanding can re-expand at a prescribed high temperature if the shell of the microspheres is formed of thermoplastic resin produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group.

(8) Heat-expanded microspheres that are capable of re-expanding and which have a specific anti-blocking agent adhered to the outer surface of their shell, quickly seal damage on a tire and exhibit high performance for supplying internal pressure to the tire.

[0023] With these findings from (1) to (8), the inventors have achieved the present invention specifically described as follows.

The first production process for heat-expanded microspheres of the present invention comprises the step of feeding a gas fluid containing heat-expandable microspheres through a gas-introducing tube having a dispersion nozzle on its outlet and fixed inside a hot gas flow, and then jetting the gas flow from the dispersion nozzle, wherein each of the heat-expandable microspheres comprises a shell

of thermoplastic resin, a blowing agent encapsulated therein having a boiling point not higher than the softening point of the thermoplastic resin, and an average particle size from 1 to 100  $\mu\text{m}$ , and then colliding the gas fluid with a collision plate fixed on the downstream portion of the dispersion nozzle to disperse the heat-expandable microspheres in the hot gas flow, and heating the dispersed heat-expandable microspheres in the hot gas flow at a temperature not lower than their expansion initiating temperature and thus expanding the heat-expandable microspheres.

[0024] The second production process for heat-expanded microspheres of the present invention comprises a step of jetting a gas fluid containing heat-expandable microspheres through at least one dispersion nozzle fixed outside a hot gas flow, and dispersing the gas fluid in the hot gas flow, wherein each of the heat-expandable microspheres comprises a shell of thermoplastic resin, and a blowing agent being encapsulated therein having a boiling point not higher than the softening point of the thermoplastic resin, and an average particle size from 1 to 100  $\mu\text{m}$ , and then heating the dispersed heat-expandable microspheres in the hot gas flow at a temperature not lower than their expansion initiating temperature to thereby expand the heat-expandable microspheres.

[0025] Heat-expanded microspheres of the present invention are produced in a process wherein heat-expandable microspheres, which comprise a shell of thermoplastic resin, and a blowing agent with a boiling point not higher than the softening point of the thermoplastic resin encapsulated in the shell, and have an average particle size ranging from 1 to 100  $\mu\text{m}$ , are heated and expanded at a temperature not lower than their expansion initiating temperature, and the heat-expanded microspheres contain not more than 5 weight percent of aggregated microspheres and not more than 5 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C.

[0026] Heat-expandable microspheres of the present invention comprise a shell of thermoplastic resin, and a blowing agent which has a boiling point not higher than the softening point of the thermoplastic resin and is encapsulated in the shell, have an average particle size ranging from 1 to 1000  $\mu\text{m}$  and an expansion coefficient above 100 %, and contain not more than 5 weight percent of aggregated microspheres and not more than 5 weight percent of microspheres having a true specific gravity not lower than 0.79 g/cc at 25°C.

[0027] The porous material composition of the present invention contains a base component, and the heat-expanded microspheres and/or the heat-expandable microspheres.

The porous molded products of the present invention are produced by molding the porous material composition.

[0028] Other heat-expandable microspheres of the present invention comprise a shell of thermoplastic resin, and a blowing agent with a boiling point not higher than the softening point of the thermoplastic resin encapsulated in the shell, and have an average particle size ranging from 1 to 100  $\mu\text{m}$ . The blowing agent contains a  $\text{C}_{2-10}$  fluorine compound which has an ether structure, and does not contain chlorine and bromine atoms. The thermoplastic resin is produced by polymerizing a monomer mixture consisting essentially of a nitrile monomer and a monomer having a carboxyl group, the

performance, the control over the re-expansion initiating temperature of heat-expanded microspheres, and the evaluation of high-speed running performance with normal internal pressure described below. The preferable weight ratio of the monomer having a carboxyl group in a monomer mixture is 20 to 80 weight percent, more preferably 40 to 80 weight percent, further preferably 50 to 80 weight percent, and most preferably 60 to 80 weight percent, considering the control over the re-expansion initiating temperature of heat-expanded microspheres, the evaluation of high-speed running performance with normal internal pressure described below, the retention of a blowing agent encapsulated in microspheres, and its blowing performance.

[0042] The monomer mixture may contain a polymerizable monomer having at least two polymerizable double bonds (a cross-linking agent) in addition to the radically polymerizable monomers. Polymerization with a cross-linking agent contributes to a reduced ratio of aggregated microspheres in heat-expanded microspheres produced by the production process of the present invention, minimum reduction of the retention of encapsulated blowing agent in microspheres after heat-expansion (retention of encapsulated blowing agent), and efficient heat-expansion of microspheres.

The retention (%) of encapsulated blowing agent in microspheres after heat-expansion in the present invention is defined as  $G_2/G_1 \times 100$ , where  $G_1$  is the retention of a blowing agent encapsulated in raw material microspheres before expansion, and  $G_2$  is the retention of blowing agent encapsulated in heat-expanded microspheres produced by heating and expanding.

[0043] The examples of cross-linking agents, but not limited to these examples, are aromatic divinyl compounds, such as divinyl benzene and divinyl naphthalene; and di(meth)acrylates, such as allyl methacrylate, triacrylformal, triallyl isocyanate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, PEG (200) di(meth)acrylate, PEG (400) di(meth)acrylate, PEG (600) di(meth)acrylate, neopentylglycol di(meth)acrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, trimethylolpropane trimethacrylate, glycerin dimethacrylate, dimethylol tricyclodecane diacrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, neopentylglycol acrylic acid benzoate, trimethylolpropane acrylic acid benzoate, 2-hydroxy-3-acryloyloxypropyl methacrylate, hydroxypivalic acid neopentylglycol diacrylate, ditrimethylolpropane tetraacrylate, and 2-butyl-2-ethyl-1,3-propanediol diacrylate. One of or a plurality of those cross-linking agents are applicable.

[0044] The preferable weight ratio of the cross-linking agents is 0.01 to 5 weight percent of the monomer mixture, more preferably 0.05 to 3 weight percent, considering the degree of cross-linking, the retention of the blowing agent encapsulated in the shell, and the heat-resistance and heat-expansion of the microspheres, though the weight ratio is not restricted within those ranges.

[0045] The polymerization initiator is not particularly limited, and known polymerization initiators

can be applied. The examples of those polymerization initiators are peroxides, such as t-butyl peroxy isobutylate, t-butyl peroxy-2-ethyl hexanoate, t-hexyl peroxy-2-ethyl hexanoate, 2,5-dimethyl-2,5-bis(2-ethyl hexanoyl peroxy) hexane, 1,1,3,3-tetramethylbutyl peroxy-2-ethyl hexanoate, t-butyl peroxy pivalate, t-hexyl peroxy pivalate, t-butyl peroxy neodecanoate, t-hexyl peroxy neodecanoate, 1-cyclohexyl-1-methylethyl peroxy neodecanoate, 1,1,3,3-tetramethylbutyl peroxy neodecanoate, cumyl peroxy neodecanoate, di-n-propyl peroxy dicarbonate, diisopropyl peroxy dicarbonate, bis(4-t-butylcyclohexyl) peroxy dicarbonate, di-sec-butyl peroxy dicarbonate, di-2-ethoxyethyl peroxy dicarbonate, di-2-ethylhexyl peroxy dicarbonate, di-3-methoxybutyl peroxy dicarbonate, 3,5,5-trimethyl hexanoyl peroxide, octanoyl peroxide, lauroyl peroxide, stearyl peroxide, succinic acid peroxide, and benzoyl peroxide; and azo compounds, such as 2,2'-azobis (4-methoxy-2,4-dimethyl valeronitrile), 2,2'-azobis isobutyronitrile, 2,2'-azobis (2,4-dimethyl valeronitrile), 2,2'-azobis (2-methyl propionate), and 2,2'-azobis (2-methyl butyronitrile). Preferable polymerization initiators are oil-soluble polymerization initiators which are soluble in radically polymerizable monomers.

[0046] The raw microspheres are produced in conventionally known processes for producing heat-expandable microcapsules.

Those processes include suspension polymerization wherein a mixture of radically polymerizable monomers, a cross-linking agent as an option, and a polymerization initiator is mixed with a blowing agent, and the resultant mixture is suspension polymerized in an aqueous medium containing a proper dispersion stabilizer.

[0047] The examples of the dispersion stabilizers in the aqueous suspension are colloidal silica, colloidal calcium carbonate, magnesium hydroxide, calcium phosphate, aluminum hydroxide, ferric hydroxide, calcium sulfate, sodium sulfate, calcium oxalate, calcium carbonate, barium carbonate, magnesium carbonate, and alumina sol. The preferable ratio of the dispersion stabilizer in the monomer mixture is 0.1 to 20 weight percent. As dispersion-stabilizing auxiliaries, polymer-type such as diethanol amine-aliphatic dicarboxylic acid condensates, gelatine, polyvinyl pyrrolidone, methyl cellulose, polyethylene oxide and polyvinyl alcohol; and emulsifiers including cationic surfactants such as alkyltrimethyl ammonium chloride and dialkyldimethyl ammonium chloride, anionic surfactants such as sodium alkyl sulfate, and amphoteric surfactants such as alkyltrimethyl betaine aminoacetate and alkyl dihydroxyethyl betaine aminoacetate may be applied. The preferable ratio of the dispersion-stabilizing auxiliary is 0.05 to 2 weight percent of the monomer mixture.

[0048] An aqueous suspension containing a dispersion stabilizer is prepared by mixing a dispersion stabilizer and an auxiliary for the dispersion stabilizer in water (for example, deionized water). The pH of the aqueous suspension during polymerization is properly determined according to the variants of a dispersion stabilizer and an auxiliary for the dispersion stabilizer. A water-soluble reducing agent may be added to the aqueous suspension, and it suppresses the formation of aggregated microspheres during polymerization. The examples of the water-soluble reducing agents are nitrites

[0059] The amount of a particulate filler adhered on the raw microspheres is not particularly limited, and is preferably 0.1 to 95 weight percent of raw microspheres before adhering the filler, more preferably 0.5 to 60 weight percent, further preferably 5 to 50 weight percent, and most preferably 8 to 30 weight percent, considering the true specific gravity of heat-expandable microspheres and the optimization of the function of a particulate filler.

[0060] A particulate filler is adhered on the outer surface of raw microspheres by mixing raw microspheres and a particulate filler. The mixing process is not particularly limited, and a device equipped with simple tools, such as a vessel and paddle blades is employable. Ordinary powder mixers for shaking or agitating powders are also applicable. The examples of powder mixers are those which can shake and agitate, or agitate powders, such as ribbon-type mixers and vertical screw mixers. Recently, highly efficient multi-functional powder mixers manufactured by combining several agitation devices, such as Super Mixer (manufactured by Kawata MFG Co., Ltd.), High-Speed Mixer (manufactured by Fukae Co., Ltd.) and New-Gra Machine (manufactured by Seishin Enterprise Co., Ltd.), have become available.

[0061] Raw microspheres are applicable as a volume retention material, for example, by filling them in a tire-and-rim assembly and expanding with heating at a temperature not lower than the expansion initiating temperature of the raw material microspheres. In addition, raw microspheres may be applied as a lightweight filler for automobile paints, expanding particles in expandable inks for wall paper and apparel design, and an expanding material for lightening resin compositions.

[0062] b. Production process for heat-expanded microspheres

The first production process for the heat-expanded microspheres of the present invention comprises the step of feeding a gas fluid containing heat-expandable microspheres through a gas-introducing tube having a dispersion nozzle on its outlet and fixed inside a hot gas flow, and then jetting the gas flow from the dispersion nozzle (jetting step), wherein each of the heat-expandable microspheres comprises a shell of thermoplastic resin and a blowing agent encapsulated therein and has a boiling point not higher than the softening point of the thermoplastic resin and have an average particle size from 1 to 100  $\mu\text{m}$ , colliding the gas fluid on a collision plate fixed on a downstream portion of the dispersion nozzle to disperse heat-expandable microspheres in the hot gas flow (dispersing step), and heating the dispersed heat-expandable microspheres in the hot gas flow at a temperature not lower than their expansion initiating temperature and thus expanding the heat-expandable microspheres (expanding step).

[0063] The production process is operated with production machines, for example, the machine having an expanding device as illustrated in Figure 1.

The expanding device comprises a gas-introducing tube (not marked with a number) being equipped with a dispersion nozzle 4 on its outlet and fixed at the center of the device; a collision plate 5 fixed on a downstream portion of the dispersion nozzle 4; a over-heating protection pipe 3 fixed around the gas-introducing tube at a proper distance; and a hot gas nozzle 1 fixed around the

over-heating protection pipe 3 at a proper distance. At the expanding device, the gas fluid containing heat-expandable microspheres 6 runs through the gas-introducing tube in the direction shown with the arrow, and the gas flow 7 runs through the space between the gas-introducing tube and over-heating protection pipe 3 in the direction shown with the arrow, for improving the dispersion of heat-expandable microspheres and to protect the gas-introducing tube and the collision plate from excessive heating. Further, the hot gas flow 8 for heating and expanding runs through the space between the over-heating protection pipe 3 and the hot gas nozzle 1 in the direction shown with the arrow. The hot gas flow 8, gas fluid 6, and gas flow 7 do not necessarily flow in the same direction, though they usually flow in the same direction. In the over-heating protection pipe 3, the cooling medium 2 for cooling is made to flow in the direction shown with the arrow.

The gas-introducing tube and/or the collision plate 5 having the over-heating protection system is preferable for controlling the generation of aggregated or fused microspheres.

The shape of the collision plate is not particularly limited, and its form may be spindle-like, conical, pyramidal, spherical, or semi-spherical form, and a combination of those forms.

[0064] At the jetting step of the first production process, the gas fluid containing heat-expandable microspheres 6 is made to flow into the gas-introducing tube equipped with the dispersion nozzle 4 on its outlet and fixed inside the hot gas flow 8, and is jetted from the dispersion nozzle 4. The gas fluid containing heat-expandable microspheres 6 is not particularly limited, so long as it is a gas containing heat-expandable microspheres. Preferable gas fluids are those comprising inert gases, such as air, nitrogen, argon, and helium containing heat-expandable microspheres.

The moisture in the gas fluid 6 is preferably not more than  $30 \text{ g/m}^3$ , more preferably not more than  $9.3 \text{ g/m}^3$ , in order to prevent poor dispersion of heat-expandable microspheres.

The flow rate of the gas fluid 6 is preferably controlled at a rate at which each heat-expandable microsphere is subjected to the same heat history as far as possible, in order to be expanded in the subsequent dispersing step, though the rate is not particularly limited.

[0065] At the dispersing step of the first production process, the gas fluid 6 is collided with the collision plate 5 fixed under the dispersion nozzle 4 for dispersing heat-expandable microspheres uniformly in the hot gas flow 8. The gas fluid 6 coming out of the dispersion nozzle 4 is introduced to the collision plate 5 with the gas flow 7 and is collided with the plate.

The same gas as that for the gas fluid 6 is applicable for the gas flow 7.

[0066] At the expanding step of the first production process, dispersed heat-expandable microspheres are heated and expanded in the hot gas flow, 8, at a temperature not lower than the expansion initiating temperature of the microspheres. Then the heat-expanded microspheres are cooled down below the softening point of the thermoplastic resin forming the shell of the heat-expandable microspheres by feeding the heat-expanded microspheres through a cooling zone or with other measures, and the heat-expanded microspheres are collected.

Ordinary solid-gas separators, such as cyclone separators or bag filters, are preferable for the



a sealant for damaged tires. Raw material microspheres or heat-expanded microspheres are rubbed together in the damaged tire, in which the volume of filled gas has decreased due to the deformation of the tire as a result of decreased internal pressure, and the temperature in the tire increases to the expansion initiating temperature of the microspheres so as to expand the microspheres, which subsequently function to increase the internal pressure of the damaged tire.

[0084] The temperature of heat-expanded microspheres filled in tires sometimes rises due to the contact between the microspheres or between the microspheres and the internal rubber surface of a tire, which is caused from the rotating motion of tires during driving of automobiles. If the temperature of heat-expanded microspheres rises above their expansion initiating temperature in running tires without damage, heat-expanded microspheres start to expand and may lose their performance for supplying internal pressure to damaged tires. In addition, the risk of losing the internal-pressure-supplying performance for damaged tires is higher in high-speed driving than in normal speed driving.

The heat-expanded microspheres produced in the production process of the present invention show satisfactory result when they are filled in tires and evaluated their running performance in driving with normal pressure and in high-speed driving with normal pressure as described below.

[0085] B. Heat-expanded microspheres

The heat-expanded microspheres of the present invention are those produced in the production process wherein heat-expandable microspheres comprising a shell of thermoplastic resin and a blowing agent with a boiling point not higher than the softening point of the thermoplastic resin being encapsulated in the shell, and having an average particle size ranging from 1 to 100  $\mu\text{m}$  are heated at their expansion initiating temperature or higher temperature. The raw heat-expandable microspheres mentioned here are preferably, but not being particularly limited, the heat-expandable microspheres described in the above "A. Production process of heat-expanded microspheres". The production process for heating and expanding heat-expandable microspheres at their expansion initiating temperature or higher temperature is preferably, but not particularly limited, the production process described in the above "A. Production process of heat-expanded microspheres".

[0086] The average particle size of heat-expanded microspheres is not particularly limited, and may be freely designed according to their application. For example, considering the retention of a blowing agent in shell and the durability of heat-expanded microspheres, a preferable average particle size ranges from 1 to 1000  $\mu\text{m}$ , more preferably 5 to 800  $\mu\text{m}$ , and most preferably 10 to 500  $\mu\text{m}$ .

[0087] The ratio of aggregated microspheres in heat-expanded microspheres is preferably not higher than 5 weight percent, more preferably not more than 1 weight percent, further preferably not more than 0.5 weight percent, and most preferably not more than 0.3 weight percent, considering the uniformity of their true specific gravity. Aggregated microspheres are identified by visual inspection through electron microscope, and their quantity can be determined by measuring the residue from